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Synthesis and Characterization of Macrocyclic-1,3-Diketones and Their Metal Chelates.

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SYNTHESIS AND CHARACTERIZATION OF MACROCYCLIC-1,3-DIKETONES AND THEIR METAL CHELATES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Thomas Charles Taylor
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DEDICATION

This work is dedicated to my mother and father,

Laura E. and A. G. Taylor,

whose guidance and encouragement

in all my endeavors

has brought me to this point.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. Eugene W. Berg for suggesting and directing this work. His guidance and assistance throughout the author's tenure at Louisiana State University was invaluable. Sincere appreciation is also extended to Dr. George R. Newkome for his assistance with matters of synthetic chemistry and literature references.

Financial assistance from the Dr. Charles E. Coates Memorial Fund donated by George H. Coates for publication of this work is gratefully acknowledged.

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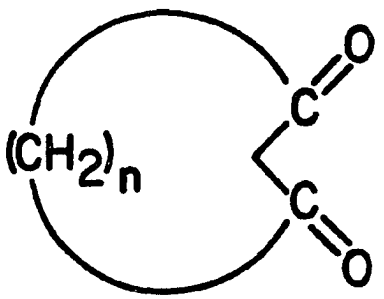
ABSTRACT

A series of five macrocyclic 1,3-diketones has been produced and characterized by infrared, nuclear magnetic resonance, mass spectroscopy and elemental analysis. The series consists of compounds of the type

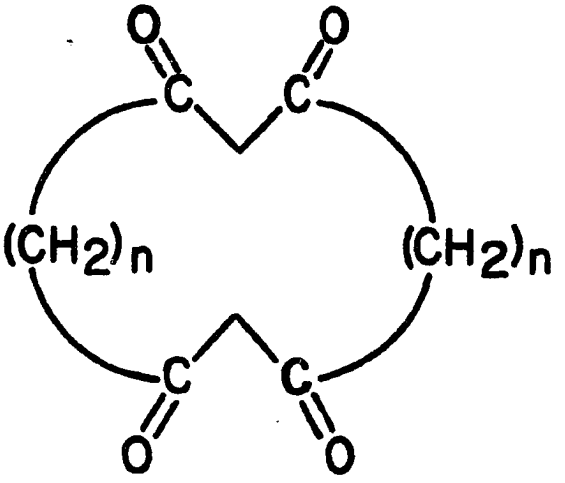


where n = 4,6,7,8 and 10.

A survey was conducted to determine the ability of these ligands to form complexes with twelve different metals. The metals used in the study were Be(II), Mg(II), Al(III), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II). Considerable selectivity was observed in the chelation reactions of these ligands, where only the ligands having 10, 11 and 13 carbon atoms formed chelates. Selectivity increased with decreasing ring size with the C_{10} ligand forming chelates only with Fe(III) and Cu(II). The chelates formed were tested for extraction in five different

solvents and for volatility in the Berg fractional sublimator. The copper chelates were further characterized by infrared and mass spectroscopy as well as by elemental and metal analysis.

An attempt was made to prepare a series of macrocyclic bis-1,3-diketones of the type



where n = 4,6,7,8 and 10 but only the n = 7 and 8 tetraketones were prepared and these in low yields. These two tetraketones were characterized by infrared and mass spectroscopy. A comparison was made of the volatility of the copper chelates of the 22 carbon tetraketone and the 11 carbon diketone.

CHAPTER ONE

INTRODUCTION

A. BACKGROUND INFORMATION

The properties of the 1,3-diketones and the corresponding metal chelates have been well documented by numerous authors.[1-9] Of these properties the volatility of the metal chelates is of special interest because it can and does provide a convenient means for separating some metals.[1,10-16] The most interesting separations have been effected by fractional sublimation and gas chromatography.

The first and the simplest of the 1,3-diketones to be studied for the formation of volatile metal chelates was acetylacetone (2,4-Pentanedione). The study was extended by modifying the substituent groups on the basic 1,3-diketone structure to see what modifications would enhance the volatility of the resulting chelates and their thermal stability. Major advantages were found in two areas of structural modification: (i) the replacement of methyl groups of acetylacetone with highly branched alkyl groups, notably tert-butyl, and (ii) the incorporation into the 1,3-diketone of perfluoroalkyl groups adjacent to either or both carbonyl

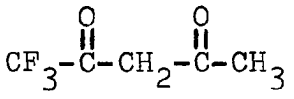
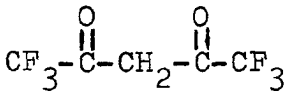
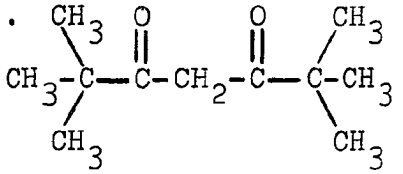
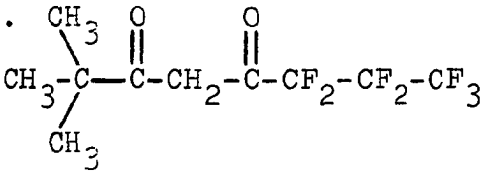
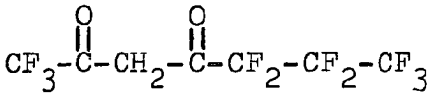
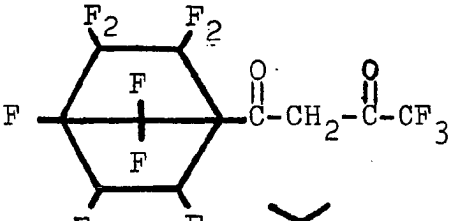
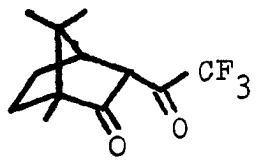
functionalities. Combinations of these two approaches have also been explored.

The most volatile and thermally stable chelates have been produced with the perfluoro substituted 1,3-diketones.[1,17-25] Trifluoroacetylacetone (1,1,1-trifluoropentane-2,4-dione) and hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoropentane-2,4-dione) have been the most widely studied and analytically developed of the fluorinated 1,3-diketones (See Table I). The increased volatility of the fluorinated 1,3-diketones over that of the nonfluorinated analogs may be due, in part, to the domination of the outer periphery of the complex by the charge density of the fluorine atoms. This concentration of charge on the outer periphery tends to reduce the van der Waals forces and intermolecular hydrogen bonding between fluorinated 1,3-diketonates. The increase in volatility of fluorinated 1,3-diketonates corresponds directly to the degree of fluorine substitution.

The replacement of methyl groups of acetylacetone with highly branched alkyl groups tends to prevent chelate hydration and thereby allows anhydrous complexes to be prepared. Although many alkyl substituted 1,3-diketonates[26] have been studied for enhanced volatility, only one ligand has shown notable promise, the symmetrical dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione) (See Table I). This ligand forms volatile chelates with the transition elements,[27] actinides,[28]

TABLE I

Some 1,3-Diketones Synthesized To Enhance Volatility of Chelates

Structure	Name
	Trifluoroacetylacetone (1,1,1-trifluoropentane-2,4-dione)
	Hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoro-pentane-2,4-dione)
	Dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione)
	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione
	1,1,1,5,5,6,6,7,7,7-decafluoro-2,4 heptanedione
	1-(perfluoro-1-bicyclo [2.2.1]heptyl)-4,4,4-trifluorobutane-1,3-dione
	Trifluoroacetyl-d-camphor

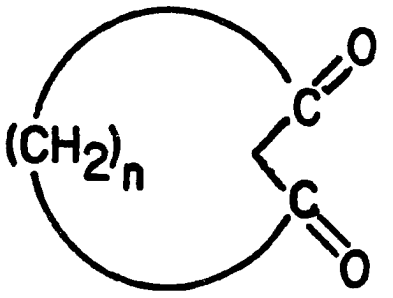
lanthanides,[29,30,31] the alkaline earths[32] and even the alkali metals.[33] Some of the rare earth complexes have been successfully separated by Berg[13] and Sievers.[29]

Sievers reported the synthesis of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione.[34] This ligand utilizes both the branched chain alkyl to prevent the formation of hydrates and the perfluoroalkyl groups to reduce intermolecular attractions and has proven useful in the gas chromatographic separation of the rare earths.[34]

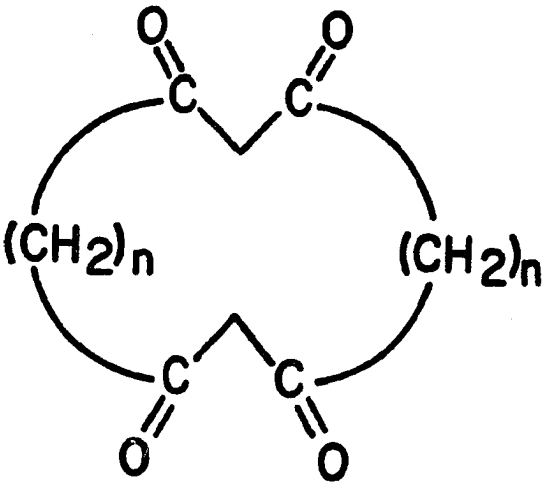
The synthesis of a novel compound, 1-(perfluoro-1-bicyclo[2.2.1]heptyl)-4,4,4-triflurobutane-1,3-dione (see Table I) was reported by Belcher.[33] The sodium chelate of this compound was formed and was found to be remarkably stable; however, it was less volatile than the hexafluroacetylacetone analog.

The work presented in this dissertation is a continuation of the search for new 1,3-diketone ligands which will produce metal chelates having greater volatility and thermal stability than those previously studied and which will show some selectivity in the chelation reaction. The goal of this study was to produce two series of macrocyclic 1,3-diketone ligands

of the type



and



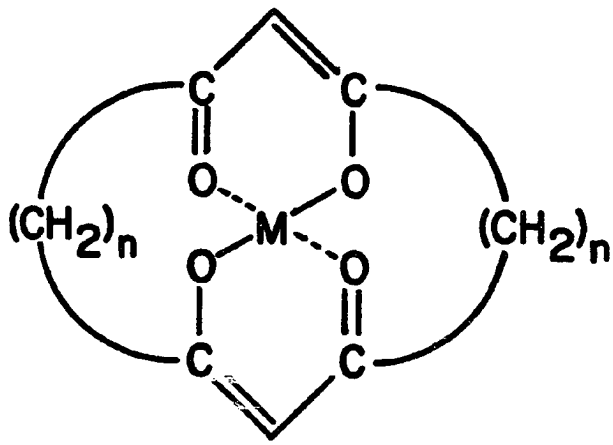
where n = 4,6,7,8, and 10.

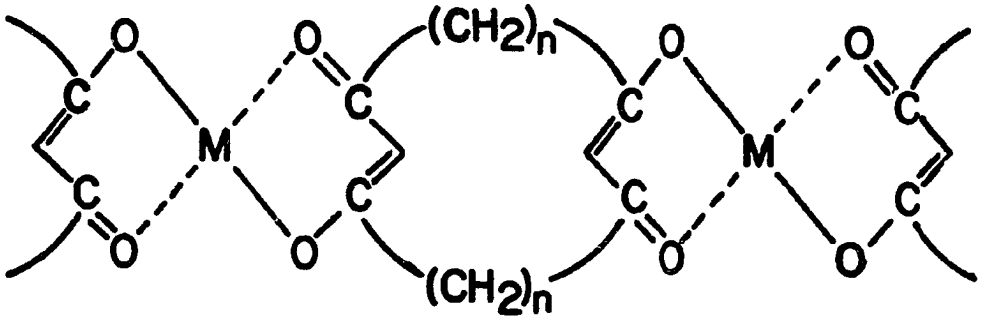
Upon chelation the macrocyclic tetraketones may form monomeric chelates or polymeric chelates depending upon whether the chelated metal ion is positioned inside or outside the ring (See Figure 1). The chelated ion of the monomeric chelates of the macrocyclic tetraketones is surrounded by a hydrocarbon shell which should minimize intermolecular interactions and hydration of the chelates.

In general the 1,3-diketones are very non-selective in their chelation reactions; however, by varying the

FIGURE 1

Possible Structures of the Macrocyclic Tetraketone Metal Chelates





size of the rings it may be possible to obtain some selectivity of chelation with these macrocyclic ligands. Molecular models indicate that the size of the macrocyclic-tetraketone ring must be approximately 22 carbon atoms in order to accommodate a metal ion within the ring.[35] It is also known that the size of the macrocyclic-diketone ring affects the enolization process and thereby the chelation process. Thus, selectivity of chelation may be realized with both the macrocyclic-tetraketones and the macrocyclic-diketones.

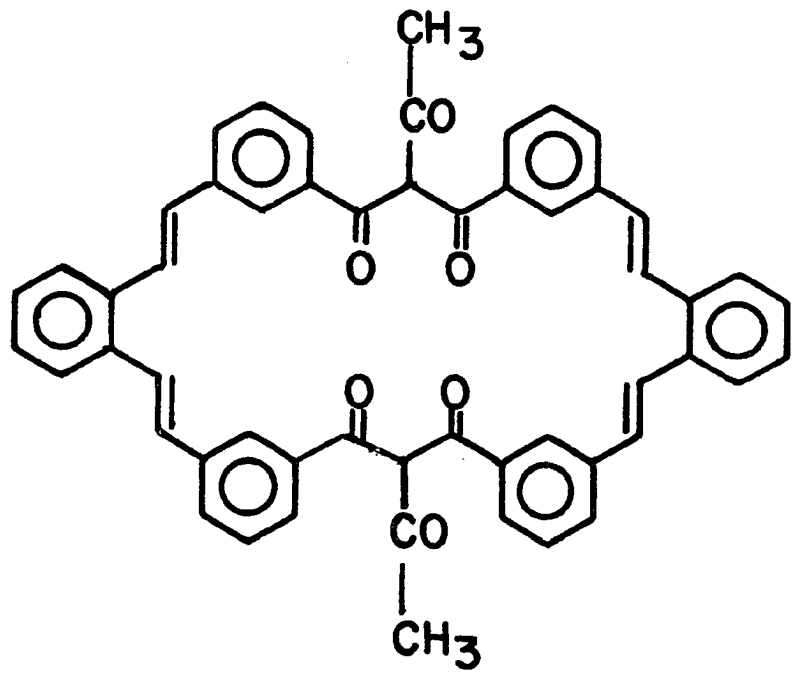
A macrocyclic-diketone and a macrocyclic-tetraketone which have the same value for n will, for a given metal ion, form two chelates which have identical molecular weights. This is true provided the tetraketone is large enough to accommodate the metal ion within the ring, thereby forming a monomeric chelate. This being the situation it is then possible to evaluate, by comparison of the diketonate with the tetraketonate, whether factors other than steric effects are important in determining the resulting properties of the alkyl substituted 1,3-diketonates.

B. MACROCYCLIC-BIS-1,3-DIKETONES

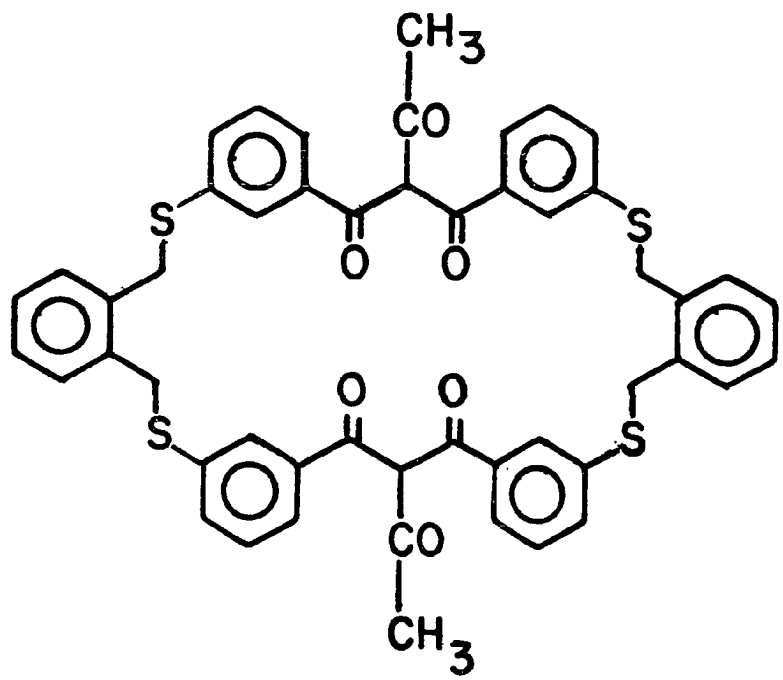
Coombs and Houghton[36] were the first to synthetically produce macrocyclic-bis-1,3-diketones. They prepared macrocyclic tetraketones I and II (Figure 2) in an attempt to produce a ligand that would selectively chelate with metal ions of a given ionic radius. Because they were

FIGURE 2

First Macrocyclic Tetraketones
to be Synthesized



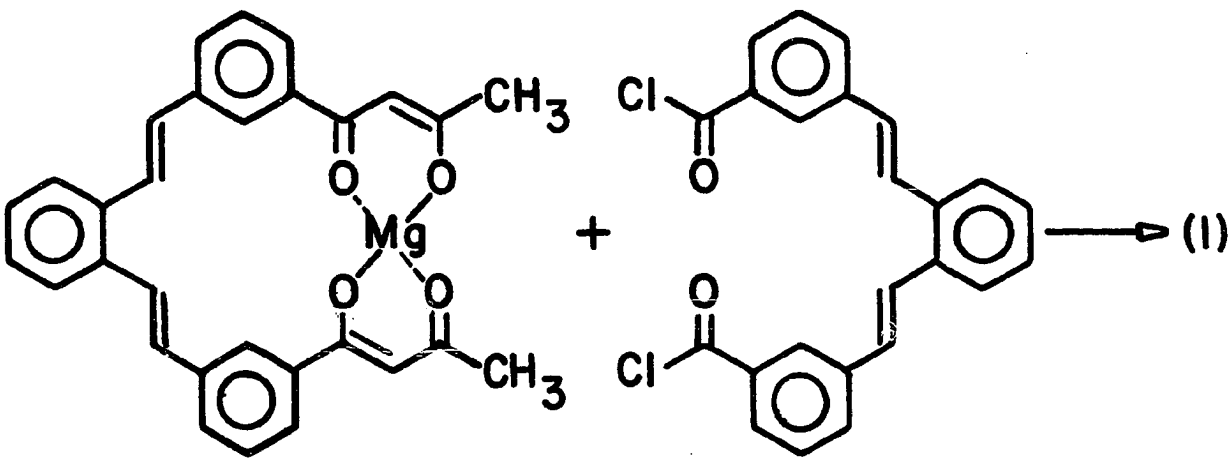
(I)



(II)

concerned only with selectivity, they utilized aromatic groups as a means of constructing rigid molecules. These compounds did not exhibit specificity of chelation, and no data were given on the volatilities of the chelates.

The synthesis of compounds I and II involved a "template" reaction in the cyclization step, in which the 1,3-diketone groups were protected and held in place by chelating them with Mg(II) ion. The ring closure was effected as follows

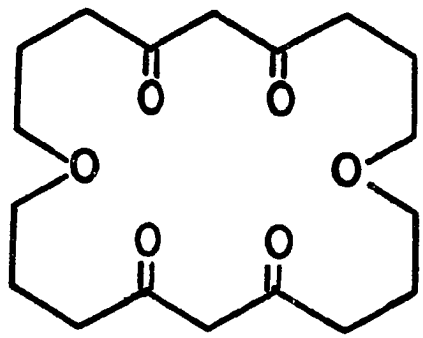


by condensing a bis(acid chloride) and magnesium chelate of the bis(1,3-diketone) in a solution of benzene and diglyme for 14 days at high dilution (26% yield).

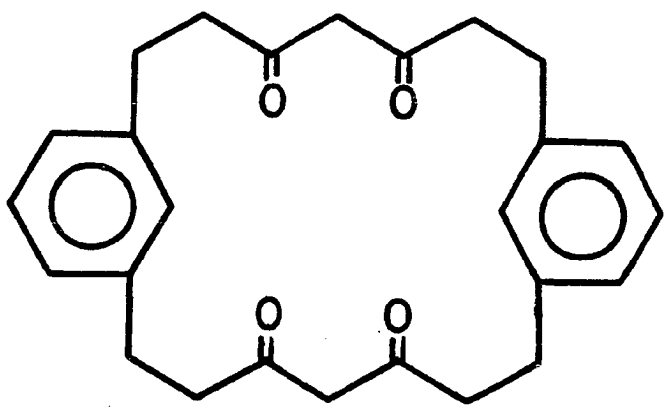
Alberts and Cram[34] reported the synthesis of macrocyclic tetraketones III and IV (Figure 3). Their synthesis involved a "template" reaction in the cyclization step. Tetraketone III could be produced from the Ca(II) but not from the Mg(II) salt, and IV could be generated from the Mg(II) but not the Ca(II) salt. These cyclic

FIGURE 3

Macrocyclic Tetraketones Synthesized
by Alberts and Cram



(III)



(IV)

1,3-diketones were found to exist completely in the enol form.

Tabushi and co-workers[38] reported the synthesis of a macrocyclic hexaketone, V, (Figure 4) which has been utilized as a specific host of the uranyl ion. They also reported the synthesis of the macrocyclic tetraketone, VI (Figure 4). No chelates of VI were reported. These ligands were synthesized from the addition products of diacid chlorides to terminal diacetylenes.

Ito and co-workers[39] reported the synthesis of macrocyclic tetraketones with 20, 22, 26, and 30 carbon atoms and their chelate formation with transition metal ions Cu(II), Ni(II), and Co(II). The synthesis is presented schematically in Figure 5.

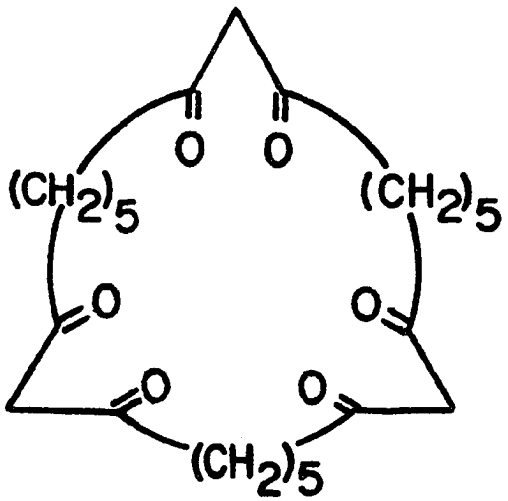
The tetrakis(trimethylsilyloxy)cycloalkadienes, VII, are derived from the silyl-acyloin condensation of aliphatic dicarboesters such as diethylnonanedioate and diethyldecanedioate. Cyclopropanation of VII with diethylzinc and methylene diiodide affords tetrakis(trimethylsilyloxy)tricycloalkanes, VIII, which are subsequently treated with Fe(III) chloride in dimethylformamide to produce the desired macrocyclic tetraketone, IX.

C. MACROCYCLIC-1,3-DIKETONES

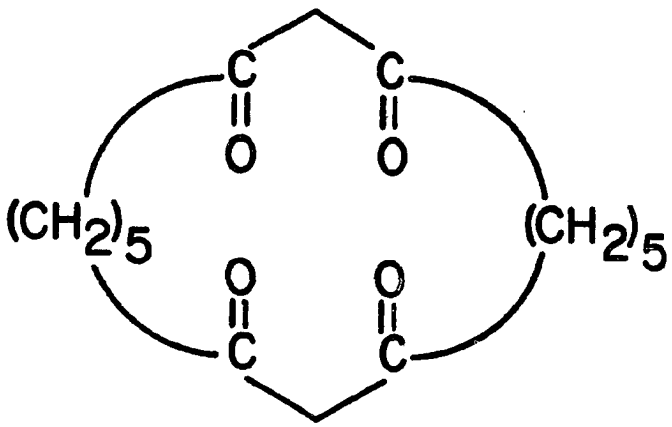
Several of the cyclic 1,3-diketones have been reported in the literature.[40-50] Lick and Schank[40] developed a three step synthesis, starting from norbor-

FIGURE 4

Macrocyclic Hexaketone and Macrocyclic Tetraketone
Synthesized by Tabushi, Kobuke and Nishiya



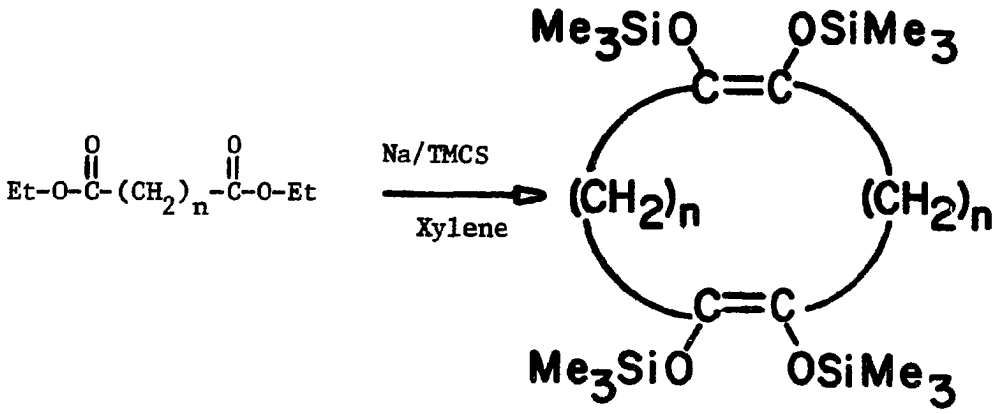
(V)



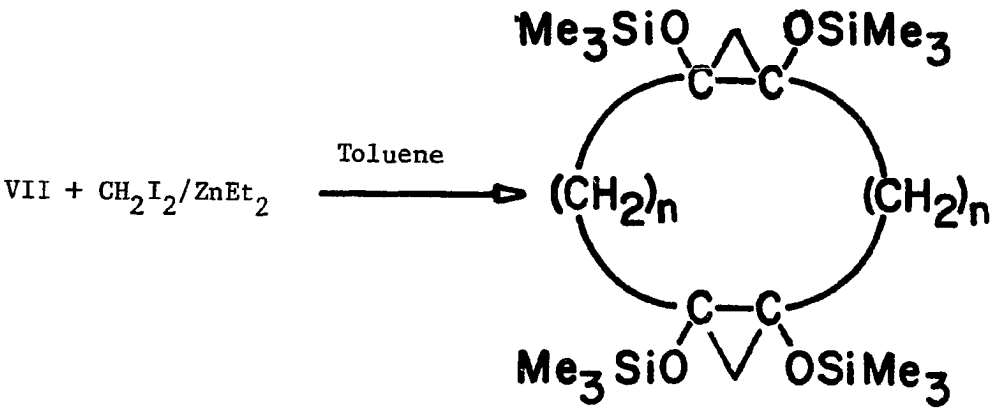
(VI)

FIGURE 5

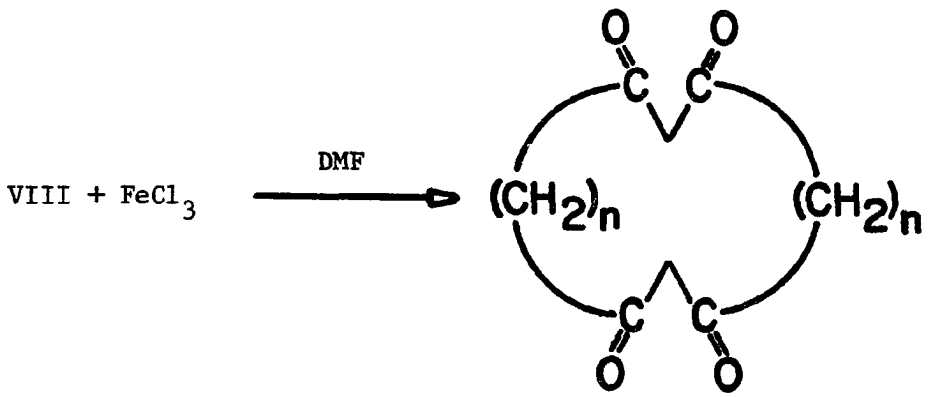
Synthetic Procedure Utilized in this Study for the Production of Macrocyclic Tetraketones



(VII)

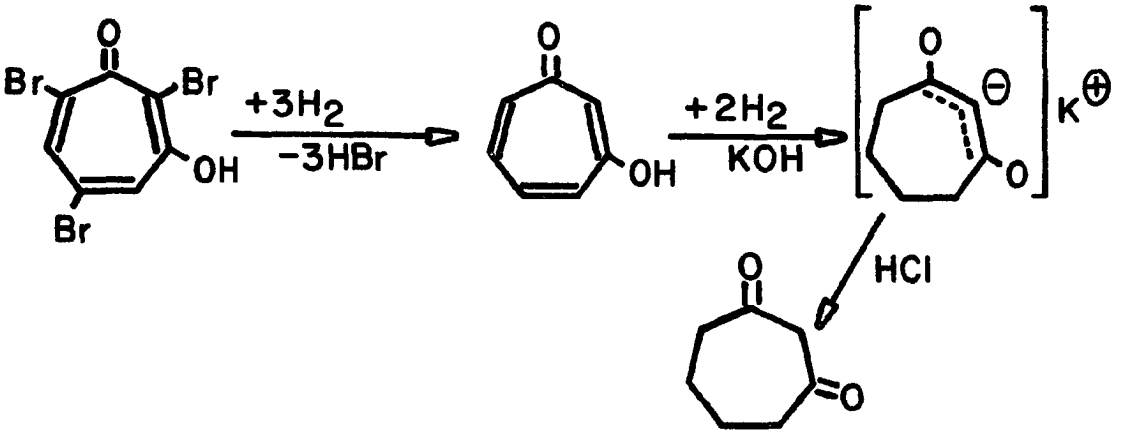


(VIII)



(IX)

nene, of 1,3-cyclopentanedione in 70% overall yield. Eistert, Haupter and Schank[41] reported the synthesis of 1,3-cycloheptanedione. The synthesis of this compound was accomplished as follows:

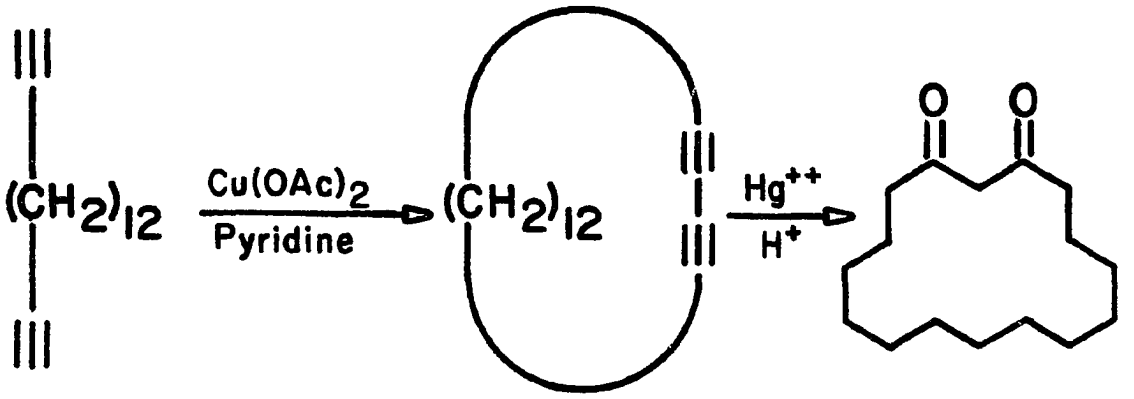


Both of these synthetic methods are specific in nature and could not readily be used in the production of a series of these compounds.

A seven step synthetic procedure was developed by Schank and co-workers[42,43] and they reported synthesis of C_8-C_{12} cyclic 1,3-diketones. A four step synthetic procedure was developed by Hunig and co-workers[44,45] and they reported synthesis of C_8-C_{15} cyclic 1,3-diketones by this method. Using the method of Hunig and co-workers Kirrman and Wakselman[46] synthesized C_{11}, C_{12}, C_{14} and C_{17} cyclic 1,3-diketones. These procedures are more general in nature but suffer from being lengthy and having rather low yields.

Stutz and Reinshagen[47] reported the synthesis of 1,3-cyclohexadecanedione. The schematic representation

of this synthesis is as follows:



This synthesis is general in nature and more straightforward; however, it is limited to macrocycles of 14 members or larger because the cyclization step with the shorter chain length terminal acetylenes yields higher order polymers.

Ito, Fujii, and Saegusa reported the production of 1,3-cycloheptanedione, 1,3-cyclononanedione[48] and 1,3-cyclopentadecanedione.[49] The synthesis is essentially the same as that developed for the production of the macrocyclic tetraketones except for reaction conditions and the use of the monomeric bis(silyloxy)enediol derived from the silyl-acyloin condensation instead of the dimer in the cyclopropanation reaction.

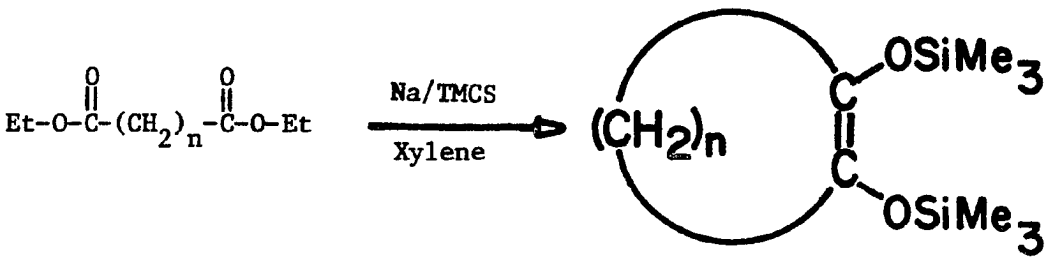
Piekut and Okamura[50] reported the synthesis of 2-methylcycloheptane-1,3-dione by Ito and co-workers' method with slight modification. In this synthesis the bis(silyloxy)enediol was methylcyclopropanated directly. Two methods of methylcyclopropanation were explored:

Zn-Cu couple/ether, reflux/40 hr. and diethylzinc/benzene, reflux/3 hr. The two procedures were equally successful.

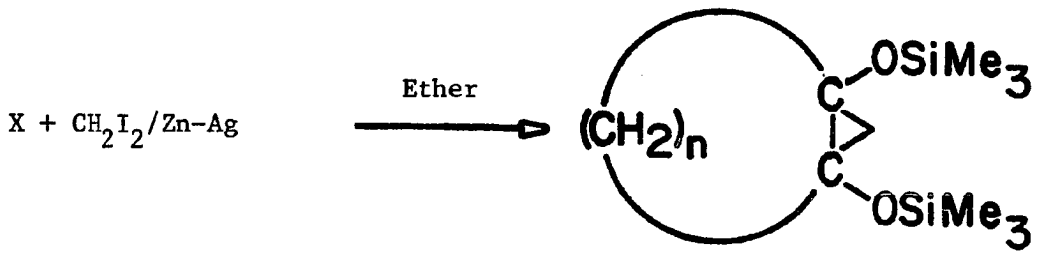
The synthetic method developed by Ito and co-workers was thought to be the most promising for the synthesis of the desired macrocyclic compounds. The synthetic procedures utilized in this study for the production of macrocyclic-tetraketones and macrocyclic-diketones are presented in Figures 5 and 6 respectively. The synthetic method utilized for the production of the macrocyclic-diketones (Figure 6) differs from that developed by Ito and co-workers in the cyclopropanation reaction. The cyclopropanation of the bis(silyloxy)enediol was effected by a modification of the traditional Simmons-Smith reaction[51] instead of by methylene iodide and diethylzinc. The modification of the classical Simmons-Smith reaction was developed by J. M. Conia[52] and utilizes a Zn-Ag couple instead of a Zn-Cu couple and the hydrolysis workup is replaced by the addition of pyridine which precipitates the zinc salts.

FIGURE 6

Synthetic Procedure Utilized in this Study for the Production of Macrocyclic Tetraketones



(X)



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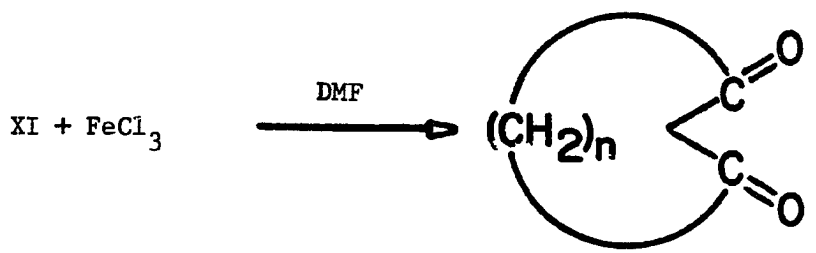


(XII)

CHAPTER TWO

EXPERIMENTAL

A. REAGENTS AND SOLVENTS

1. Reagents

Adipic acid $HOOC-(CH_2)_4-COOH$

The reagent, supplied by Fisher Scientific Company, was used without further purification.

Suberic acid $HOOC-(CH_2)_6-COOH$

The reagent, supplied by Matheson, Coleman and Bell, was used without further purification.

Azelaic acid $HOOC-(CH_2)_7-COOH$

The reagent, supplied by Aldrich, was used without further purification.

Sebacic acid $HOOC-(CH_2)_8-COOH$

This reagent was supplied by Eastman and was used without further purification.

Ethyl Alcohol

This reagent was supplied by U.S. Industrial Chemical Company. The reagent quality, absolute pure ethyl alcohol was used.

Sodium

Elemental sodium was obtained from Matheson, Coleman and Bell. Reagent grade sodium was used without

further purification.

Trimethylchlorosilane (TMCS)

Technical and reagent grades, obtained from Matheson, Coleman and Bell, were used without further purification.

Silver Acetate

The 99.5% powder was obtained from Matheson, Coleman and Bell and was used without further purification.

Zinc

Reagent grade grannular zinc (30 mesh) was obtained from Matheson, Coleman and Bell and was used as received.

Diethyl Zinc

This reagent was obtained from Aldrich as a 25 wt. % solution in toluene.

Diiodomethane

The reagent, supplied by Matheson, Coleman and Bell, was used without further purification.

Ferric Chloride

The anhydrous powder, supplied by Matheson, Coleman and Bell, and Aldrich, was used as received.

Metals

All of the metals used for the study of chelates and chelate formation were supplied by various vendors as the nitrate salts, with the exception of palladium which was obtained as the chlorocomplex. These salts were used without further purification.

2. Solvents

Toluene

Reagent grade Toluene was supplied by Matheson, Coleman and Bell. This solvent was dried over metallic sodium and filtered before use.

Diethyl Ether

The anhydrous, reagent grade solvent was supplied by Mallinckrodt and Matheson, Coleman and Bell and was used as received.

N,N-Dimethylformamide (DMF)

Aldrich supplied the spectrophotometric grade solvent which was used without further purification.

Chloroform

Bulk chloroform supplied by Dow Chemical was used without further purification.

B. INSTRUMENTS AND MEASUREMENTS

1. Nuclear Magnetic Resonance Spectroscopy

All the spectra provided were recorded on the Bruker Spectrospin 200 MHz FT-NMR spectrometer. Sample solutions of 10% by volume (approximate) in deuterated chloroform were used for all spectra. All the chemical shifts are given in delta (δ). The spectra are collectively listed in Appendix I, page 68.

2. Infrared Spectroscopy

The infrared spectra shown were recorded with the Beckman IR-9 (linear wavenumber) spectrophotometer.

Samples were prepared as thin films or as potassium bromide pellets. The spectra are collectively listed in Appendix II, page 85.

3. Chelation and Extraction Survey

The chelation survey was conducted using 5.0% aqueous solutions of the metal nitrates containing 5% sodium acetate. The one exception was palladium, which was obtained as the chlorocomplex $PdCl_4^{2-}$. The ligands were used in the form of a 5% solution in ethanol.

A few drops of acetate buffered metal nitrate solution were placed in the depression of a spot plate, to which a few drops of ligand solution were added. The reagents were mixed and allowed to stand for 10-15 minutes. The formation of a precipitate indicated chelation had taken place. The absence of a precipitate indicated that no neutral chelate species was formed. Each precipitate was checked for extraction in five different solvents using a Carlton pipette.

4. Fractional Sublimation Determinations

Each of the metal chelates produced in the study was placed in the Fractional Sublimator and checked for volatility. The apparatus and procedures were those described by Berg and Hartlage.[11,12] The experimental conditions employed and the sublimation recrystallization zone temperatures are given in Table II.

TABLE II

Fractional Sublimation Data for
Various Macrocyclic-1,3-Diketone Metal Chelates

Chelate	Max. T °C	Pressure mm (Hg)	Crystal Zone Temperature
C_{10}-Fe(III)	185	1.0	decomposed
C_{10}-Cu(II)	190	1.0	132-118
C_{11}-Fe(III)	170	1.0	decomposed
C_{11}-Co(II)	178	1.0	decomposed
C_{11}-Ni(II)	183	1.0	decomposed
C_{11}-Cu(II)	198	1.0	130-115
C_{11}-Pd(II)	190	1.0	decomposed
C_{13}-Fe(III)	180	1.0	135-110
C_{13}-Co(II)	183	1.0	135-90
C_{13}-Ni(II)	190	1.0	140-125
C_{13}-Cu(II)	205	1.0	170-130
C_{13}-Zn(II)	195	1.0	100-80
C_{13}-Pd(II)	187	1.0	decomposed
C_{13}-Mn(II)	177	1.0	decomposed
C_{13}-Mg(II)	191	1.0	decomposed
C_{13}-Cd(II)	189	1.0	decomposed

5. Carbon-Hydrogen Analyses

Carbon-hydrogen analyses were provided by Mr. Ralph Seab, Louisiana State University.

6. Mass Spectroscopy

The mass spectra were obtained by Mr. Don Patterson of Louisiana State University. The instrument used was the Hewlett Packard 5985 GC/MS System.

7. Copper Analysis

The copper chelates were dissolved in chloroform and the copper extracted into 10% H_2SO_4. The acid solution then was electrolytically analyzed for copper with a Sargent-Slomin analyzer. This instrument allowed for the electrodeposition of the copper from the acid medium.

C. SYNTHESIS OF THE MACROCYCLIC 1,3-DIKETONES

1. Esterification

The esterification reaction was conducted in the same manner in every case. Into a 1000 mL round-bottomed flask was placed 100 g of the appropriate acid (adipic, suberic, etc.). Then 100 g (127 mL) of absolute ethyl alcohol, 250 mL of sodium-dried toluene and 40 g (22 mL) of concentrated sulfuric acid were added (the latter cautiously) in succession. A reflux condenser was attached to the flask and the mixture refluxed gently for 24 to 48 hours. The reaction mixture was allowed to cool

and then poured into an excess of water (2-3 volumes). The toluene layer was separated and washed with saturated sodium bicarbonate solution until effervescence ceased, then with water. The organic layer was then allowed to dry over anhydrous sodium sulfate. Most of the toluene was removed on a rotary flash evaporator and the residue distilled under reduced pressure to yield the pure diethyl ester of the starting acid. In each case the yield was greater than 90%.

2. Silyl-Acyloin Condensation (monomer formation)[53,54]

Into a 2000 mL three necked, round bottomed flask equipped with a condenser, high speed stirrer (stir-o-vac) and a nitrogen inlet/addition port was placed 1000 mL of sodium dried toluene and 2 g atoms (46 g) of elemental sodium. The toluene was brought to reflux (by means of a heating mantle) under a gradual flow of dry N_2 and the stirrer was turned on and operated at a high speed in order to form a fine dispersion of molten sodium in the refluxing toluene. Carefully, 2.2 moles (280 mL) of trimethylchlorosilane (TMCS) was added by means of a 50 mL syringe through the septum equipped side-arm on the N_2 inlet. The surface of the sodium turned dark after the addition of the TMCS. The speed of the stirrer was reduced and 0.5 mole of the appropriate ester was added dropwise by means of a 50 mL syringe and syringe pump. The addition of the ester was at a rate of 0.34 mL/min.

which was controlled by the setting on the syringe pump. After the addition of the ester was complete, the mixture was allowed to reflux with stirring under an atmosphere of nitrogen for 10-12 hours. The heating mantle was turned off and the mixture allowed to cool. After cooling to room temperature the mixture was maintained under a N_2 atmosphere and allowed to settle with the stirrer off. After settling for about 30 min. the mixture was filtered through a bed of Celite 545 on a medium porosity fritted glass funnel (350 mL) (larger would be better). The purple residue was then washed with absolute diethyl ether and the washings added to the filtrate. Care should be taken in handling the purple residue since it may contain unreacted sodium and it should be disposed of in an appropriate manner. The solvent was removed from the filtrate on a rotary flash evaporator and the residue distilled under reduced pressure. The yield of this reaction was greatest for the shortest chain length due to increased formation of the acyloin dimer. The yields obtained, noted by ring size, are as follows: C_6 - 96%, C_8 - 94%, C_9 - 90%, C_{10} - 85%, C_{12} - 80%. The compounds were all colorless liquids and gave the following carbon-hydrogen analyses:

ring size	molecular formula	%Calculated C	%Calculated H	%found C	%found H
C_6	$C_{12}H_{26}O_2Si_2$	55.76	10.14	55.46	9.91
C_8	$C_{14}H_{30}O_2Si_2$	58.68	10.55	58.53	10.40
C_9	$C_{15}H_{32}O_2Si_2$	59.94	10.73	59.80	10.65

ring size	molecular formula	% Calculated C	% Calculated H	% found C	% found H
C_{10}	$C_{16}H_{34}O_2Si_2$	61.08	10.89	61.00	11.30
C_{12}	$C_{18}H_{38}O_2Si_2$	63.09	11.18	63.10	11.22

The nuclear magnetic resonance, infrared and mass spectra of these compounds appear in appendices I, II and III respectively.

3. Cyclopropanation of the Silyl-Acyloin Monomer[51,52]

To a hot (50-60°C) stirred solution of silver acetate (200 mg) in acetic acid (250 mL), granular zinc (30 mesh, 34 g, 0.52 g atom) was added in one portion. The mixture was stirred for 30 sec., and the zinc-silver couple formed was isolated by decantation and washed with ether (5 x 100 mL). Anhydrous ether (250 mL) was then poured onto the product. The couple was used directly in the cyclopropanation reaction.

To the ethereal suspension of zinc-silver couple, methylene iodide (68 g, 0.26 mol) was added dropwise with stirring while the mixture was maintained at gentle reflux. Stirring was continued without external heating until refluxing ceased (approximately 1 hour). The silyl-acyloin monomer (0.20 mole) was added dropwise over 15 minutes, and the mixture was allowed to reflux for 24 hours. The mixture was then cooled and filtered and the residue washed with portions of ether. The washings and the filtrate were placed in an 800 mL beaker and stirred while 40 mL of pyridine were added dropwise. The

resultant precipitate was removed by filtration and washed with ether. The filtrate and washings were combined and a little pyridine was added dropwise until no more precipitate formed. After filtration, the ether was removed on a rotary flash evaporator. The residue was checked by 200 MHz nmr to determine the extent of reaction. If reaction had not gone to completion, fresh zinc-silver couple was prepared and the reaction run as before. Once it had been determined by nuclear magnetic resonance spectroscopy that the reaction had gone to completion, or nearly so, the residue was distilled under reduced pressure. In this manner the final yield of cyclopropanated product was in every instance 80% or better. The products were all colorless liquids and gave the following carbon-hydrogen analyses:

Molecular formula	% calculated C	H	% found C	H
$C_{13}H_{28}O_2Si_2$	57.29	10.36	57.13	10.25
$C_{15}H_{32}O_2Si_2$	59.94	10.73	59.78	10.61
$C_{16}H_{34}O_2Si_2$	61.08	10.89	61.00	10.75
$C_{17}H_{36}O_2Si_2$	62.13	11.04	62.01	10.89
$C_{19}H_{40}O_2Si_2$	63.98	11.30	63.83	11.21

The nuclear magnetic resonance and infrared spectra for these compounds appear in appendices I and II respectively.

4. Ferric Chloride Oxidation[48,49]

Under a nitrogen atmosphere 0.2 mole of the cyclopropanated product was added dropwise to a stirred

solution of 0.4 mole (64.88 g) of anhydrous Fe(III) chloride in 300 mL of DMF at room temperature. The mixture was then heated at 60-65°C for 3 hours. The reaction mixture was cooled and then poured into 10% aqueous HCl and extracted repeatedly with chloroform. The chloroform extracts were combined and washed with 50% aqueous HCl and with water and dried over anhydrous sodium sulfate. The chloroform solution was filtered and concentrated on a rotary flash evaporator. The residue was distilled at reduced pressure to furnish the cycloalkane-1,3-dione. The yields, according to ring size of the resultant diketones, were: C_7 - 68%; C_9 - 75%; C_{10} - 79%; C_{11} - 83%; C_{13} - 87%. The C_{11} diketone was a crystalline solid at room temperature and the rest were colorless or lightly colored liquids. The following carbon-hydrogen analyses have been obtained:

ring size	molecular formula	% Calculated C	% Calculated H	% found C	% found H
C_7	$C_7H_{10}O_2$	66.65	7.99	65.75	8.71
C_9	$C_9H_{14}O_2$	70.10	9.15	69.22	9.45
C_{10}	$C_{10}H_{16}O_2$	71.39	9.59	71.13	9.61
C_{11}	$C_{11}H_{18}O_2$	72.49	9.95	72.23	10.14
C_{13}	$C_{13}H_{22}O_2$	74.24	10.54	74.32	10.63

The nuclear magentic resonance, infrared and mass spectra for these compounds appear in appendices I, II and III respectively.

5. Metal Chelates of the Macrocyclic Diketones

The manner in which the chelates were formed is given on page 27. The copper chelates were characterized by infrared and mass spectroscopy (spectra are given in appendices II and III respectively) and by carbon-hydrogen and copper analyses. The only ligands which formed chelates with copper were the C_{13}, C_{11} and C_{10} macrocycles. The results of the analyses of these chelates are as follows:

ligand	molecular formula	% calculated C	% calculated H	% found C	% found H
C_{10}	$C_{20}H_{30}O_4Cu$	60.36	7.60	60.23	7.86
C_{11}	$C_{22}H_{34}O_4Cu$	62.02	8.04	61.94	8.29
C_{12}	$C_{26}H_{42}O_4Cu$	64.77	8.78	64.36	8.97
	Copper Analysis				
C_{10}	$C_{20}H_{30}Cu$	15.96 %		15.94 %	
C_{11}	$C_{22}H_{34}Cu$	14.91 %		14.74 %	
C_{13}	$C_{26}H_{42}O_4Cu$	13.18 %		13.28 %	

D. SYNTHESIS OF THE MACROCYCLIC-BIS-1,3-DIKETONES

1. Esterification

The procedure for the production of the esters required is given on page 29.

2. Silyl-Acyloin Condensation (dimer formation)[39]

Into a 2000 mL three necked, round bottomed flask equipped with a condenser, high speed stirrer (stir-o-vac) and a nitrogen inlet/addition port was placed

800 mL of sodium dried toluene and 2 g atoms (46 g) of elemental sodium. The toluene was brought to reflux under a gradual flow of dry N_2 and the stirrer operated at a high speed. Once a fine dispersion of sodium had been produced the speed of the stirrer was reduced and 2.2 moles (280 mL) of TMCS was added cautiously by means of a 50 mL syringe through the side-arm on the N_2 inlet equipped with a septum. A few milliliters of ester were added dropwise by means of a 50 mL syringe and syringe pump. After the reaction had been initiated the remainder of the 0.5 mole of ester was added at as fast a rate as the exothermic nature of the reaction would allow. After the addition of the ester was complete the mixture was stirred and refluxed overnight under a gradual flow of nitrogen. The mixture then was allowed to cool to room temperature and filtered through a bed of Celite 545 on a medium porosity fritted glass funnel. The residue was washed with ether and the washings and filtrate combined (The same precautions given on page 31 apply to the purple residue obtained here). The solvent was stripped on a rotary flash evaporator and the residue distilled at reduced pressure. The distillation was stopped once the temperature reached 200°C. The distillate was the silyl-acyloin dimer. Upon standing a few days the viscous oil solidified into a crystilline solid. A portion of this material was recrystalized from toluene and analyzed. The results

of these analyses are as follows:

molecular formula	melting pt.	% calculated C	% calculated H	% found C	% found H
$C_{30}H_{64}O_4Si_4$	65-66°C (lit. 64-67°C)	59.94	10.73	59.99	10.59
$C_{32}H_{68}O_4Si_4$	89-90°C (lit. 90-90.5°C)	61.08	10.89	60.97	10.89

The nuclear magnetic resonance, infrared and mass spectra for these compounds appear in appendices I, II and III respectively.

3. Cyclopropanation of the Silyl-Acyloin Dimer[39]

Under a nitrogen atmosphere, 40.2 g (150 mmol) of methylene diiodide was added dropwise to a stirring mixture of 26 mmol of the silyl-acyloin dimer and 15.7 g (130 mmol, 67.6 mL of a 25 wt. % solution in toluene) of diethylzinc and 40 mL of sodium dried toluene at room temperature. The mixture was heated at reflux for 3 hours. The reaction mixture was cooled in an ice water bath and then poured into 200 mL of a cold, saturated ammonium chloride solution with stirring (The solution should be contained in an 800 mL beaker and the reaction mixture added slowly since copious foaming occurs). The mixture was transferred to a sepratory funnel and extracted repeatedly with chloroform. The chloroform extracts were back washed with saturated NH_4Cl, then with water and dried over anhydrous sodium sulfate. The chloroform solution was filtered and then concentrated on a rotary flash evaporator and the concentrate was distilled under reduced pressure. A viscous oil remained in the still pot

and exhibited an absorption band in its infrared spectrum at 3070 cm^{-1} characteristic of a cyclopropane ring at the expense of a band at 1665 cm^{-1} ascribable to the carbon-carbon double bond of the starting material. This viscous liquid was subjected to the ferric chloride oxidation reaction without further purification.

4. Ferric Chloride Oxidation

The cyclopropanated product (19 mmol) was dissolved in a small amount of ether and the solution added dropwise to a solution of 76 mmol (12.4 g) of anhydrous ferric chloride in 50 mL of DMF at room temperature. The mixture then was heated with stirring at 60-65°C for 4 hours. The reaction mixture was poured into 10% HCl solution and extracted with chloroform. The chloroform extract was washed with 50% HCl and then with water and then dried over anhydrous sodium sulfate. The chloroform solution then was filtered and concentrated. The residue was dissolved in bulk ethanol which had been buffered with sodium acetate. The ethanol solution was filtered and treated with an excess of cupric nitrate solution. The copper chelate of the tetraketone precipitated and was collected and washed on a medium porosity fritted glass funnel. The precipitate was washed successively with ethanol, acetone and ether and then was dissolved in chloroform and filtered. The chloroform was evaporated and a portion of the blue crystalline copper chelate was collected for study and analysis. The

remainder of the copper chelate was dissolved in chloroform and treated with 50% HCl. The aqueous layer was extracted a few times with chloroform and the chloroform extracts washed with water and dried over anhydrous sodium sulfate. The chloroform solution was filtered and evaporated yielding the pure tetraketone which was subsequently analyzed. The results of these analyses are as follows:

ring size	molecular formula	% Calculated C	% Calculated H	% found C	% found H
20	$C_{20}H_{32}O_2$	71.39	9.95	71.28	9.60
22	$C_{22}H_{36}O_2$	72.49	9.95	72.53	9.77

The results of the analyses of the copper chelates of these ligands are as follows:

ring size	molecular formula	% Calculated C	% Calculated H	% found C	% found H
20	$C_{20}H_{32}O_2Cu$	60.36	7.60	59.60	7.47
22	$C_{22}H_{36}O_2Cu$	62.02	8.04	61.73	8.30

The infrared and mass spectra of these compounds appear in appendices II and III respectively.

CHAPTER THREE

DISCUSSION

A. SYNTHESIS PROCEDURES

1. Macrocyclic 1,3-Diketones

a. Esterification

The starting materials for these synthetic procedures were the α,ω-diacids which were subsequently converted to the corresponding α,ω-diesters. The diethyl esters were used in this study; however, the dimethyl esters perform equally well. The diethyl esters have a slight advantage over the dimethyl esters in that some of the dimethyl esters are crystalline solids at room temperature and the diethyl esters are all liquids and, therefore somewhat easier to handle. The esterification reactions proceeded smoothly in high yield and no problems were encountered with these reactions.

b. Silyl-Acyloin Condensation for Monomer Production

The production of the silyl-acyloin monomer can best be accomplished under conditions of reasonably high dilution. The reason being, of course, that the lower the concentration of diester the greater the probability that one end of the ester will condense with the

other end of the same molecule rather than condensing with the end of a second molecule of ester to form a dimer or higher polymer. Because the reaction takes place on the surface of the sodium, the greater the surface area of the sodium the greater the probability of reaction and the higher the reaction rate. For this reason a very high surface area of sodium is ensured by the production of a fine dispersion of molten sodium in refluxing toluene using a high speed stirrer (Stir-o-vac).

The acyloin reaction is exothermic in nature and some care should be exercised to keep the reaction under control. The dropwise addition of the ester is one way to insure that a smooth, controlled reaction occurs. Ruhlmann[53] utilized a procedure in which all of the ester was added to the reaction mixture in one portion but this procedure has resulted in serious fires as indicated by Bloomfield.[54] There is also the increased chance of dimers and higher polymers being formed by this procedure.

There seems to be an "induction" period for the silyl-acyloin condensation. What is meant by "induction" period is that reaction does not seem to take place with the dropwise addition of the ester until 2-3 mL of ester have been added. Then, vigorous refluxing occurs simultaneously with the appearance of a purple color on the surface of the sodium. Once the vigorous refluxing subsides the ester may be added dropwise in a continuous manner and the reaction proceeds smoothly. The reason for, and the nature of this "induction" period are not known.

Bloomfield[54] indicates that the acyloin condensation should not be conducted with trimethylchlorosilane that has not been previously distilled, preferably from calcium hydride, under nitrogen. Trimethylchlorosilane may contain some dimethyldichlorosilane as an impurity. The dihalosilane hydrolyzes more readily than does TMCS. In at least one laboratory the use of this reagent without prior purification has been followed by explosions and injury to at least two people. The explosions occurred in reactions run on larger than a 0.1 mole scale, using undistilled TMCS and following the procedure of Ruhlmann. The problems encountered were most likely due to the procedure used rather than the purity of the TMCS. The acyloin condensation reactions reported in this work were conducted on a 0.5 mole scale with undistilled TMCS without any problems as long as the dropwise addition of the ester was observed.

c. Cyclopropanation of the Silyl-Acyloin Monomer

There have been a number of variations of the cyclopropanation reaction developed,[51] all of which involve a reactive, yet discriminating, organozinc intermediate. The procedure utilized for the cyclopropanation of the silyl-acyloin monomer is a variation of the classic Simmons-Smith reaction. This procedure was developed by J. M. Conia[52] and it varies from the traditional Simmons-Smith reaction in that a zinc-silver couple is used instead of a zinc-copper couple. This

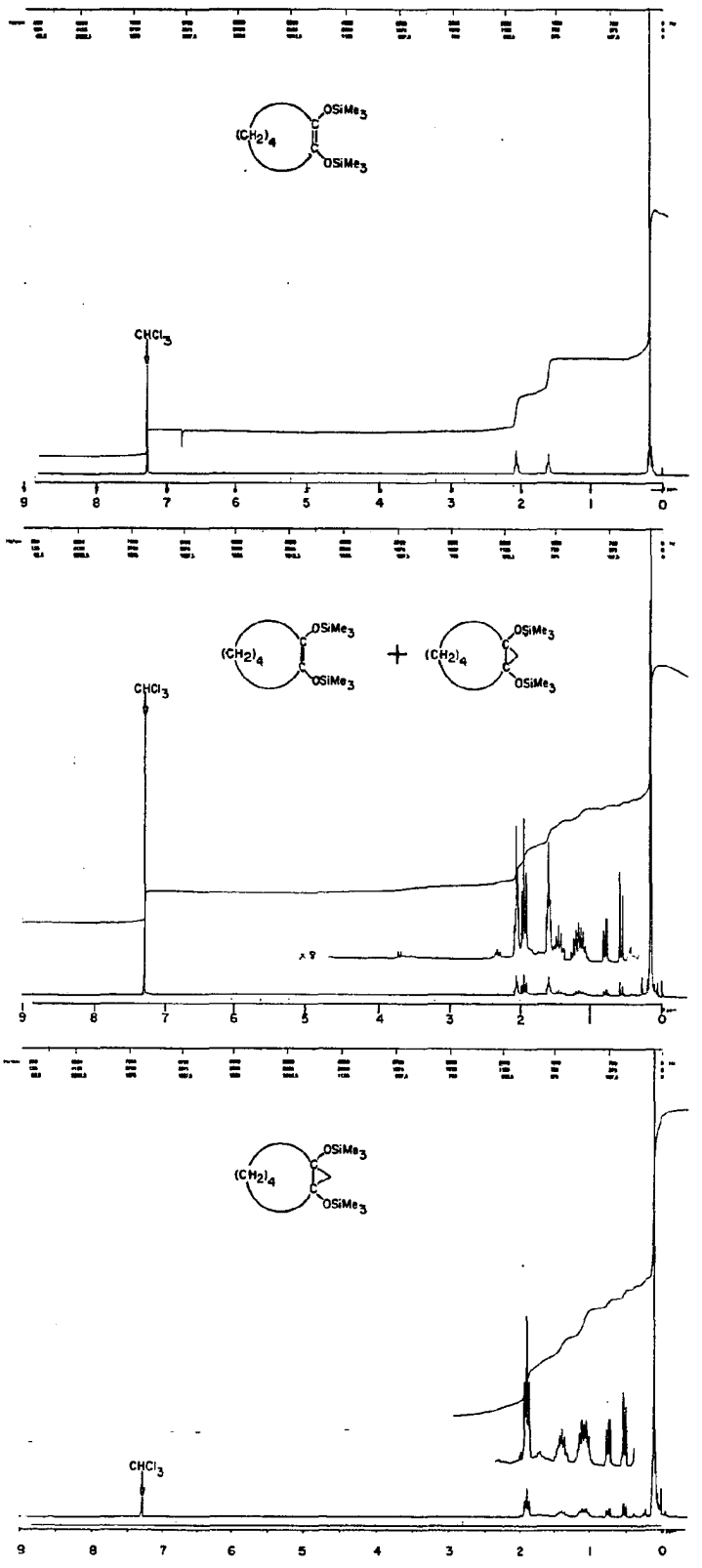
modification of the reaction is not essential in the case of the cyclopropanation of silyl ethers. However, the use of a zinc-silver couple offers advantages over the use of the zinc-copper couple because it is more reactive towards diiodomethane, it gives slightly better yields of siloxycyclopropane, a large excess of the reagent (CH_2I_2, Zn/Ag) is not necessary to complete the reaction and the reaction time is reduced.

The usual workup of the reaction mixture by acid hydrolysis is not convenient in the cyclopropanation of silyl ethers, because the cyclopropanation products can undergo ring opening and any unreacted olefin will be destroyed. Therefore the final hydrolysis of the reaction mixture was replaced by the addition of an amine, e.g., pyridine, to remove zinc salts. The addition of pyridine circumvents the problems encountered with hydrolysis and allows the reaction mixture to be analyzed by nuclear magnetic resonance spectroscopy to determine the extent of reaction.

The determination of the extent of reaction was done simply by obtaining the nmr spectra of the reaction mixture from the Bruker Spectrospin 200 MHz FT-NMR. The trimethylsilyl protons of the starting olefin and the cyclopropanation product give two singlets with chemical shifts differing by 2Hz (0.01 ppm) (see Figure 7). The singlet furthest upfield is due to the starting olefin. A comparison of the intensities of these two singlets gives the relative amount of starting material and

FIGURE 7

200 MHz Nuclear Magnetic Resonance Spectra
of 1,2-Bis(trimethylsilyloxy)cyclohexene,
1,6-Bis(trimethylsilyloxy)bicyclo[4.1.0]heptane
and a Mixture of Both



product in the reaction mixture. If the reaction has not gone far enough towards completion, the cyclopropanation reaction can be run again on this partially reacted mixture.

The nmr spectra of the cyclopropanation product (Figure 7) also exhibits a pair of doublets centered at approximately 0.675 ppm. These doublets are due to the cyclopropane protons which are not equivalent and are coupled to one another.

d. Ferric Chloride Oxidation

The ferric chloride oxidation of the cyclopropanation product produced from the cyclopropanation reaction on the silyl-acyloin monomer proceeded smoothly and in good yield. The best results were obtained when the cyclopropanation product was as free of zinc salts and zinc-pyridine complex as possible. The zinc salts and the zinc-pyridine complex were removed by repeated filtration of the cyclopropanation reaction mixture. Usually some of the zinc-pyridine complex remained in the filtrate and gradually precipitated from solution but as long as the amount of zinc in the mixture was low, the oxidation reaction proceeded in good yield.

An acid workup of the mixture was necessary to extract the iron from the reaction mixture. The mixture was extracted first with 10% HCl (10 mL conc. HCl diluted to 100 mL) and then with 50% by volume concentrated HCl. The second extraction was required, especially in the case

of the larger diketones, to extract the iron which was most likely complexed by the diketone present in the reaction mixture. The larger diketones, especially C_{13}, held the "complexed" iron in the chloroform phase rather tenaciously.

2. Macrocyclic Bis-1,3-Diketones

a. Esterification

The esterification procedure was discussed in section 1a, page 40.

b. Silyl-Acyloin Condensation for Dimer Production

The manner in which the acyloin condensation reaction was run when the dimer was the desired product was slightly different from that when the monomer was the desired product. The difference was in the manner in which the ester was added to the other reactants. The ester was added dropwise at as fast a rate as the exothermic nature of the reaction would allow because a higher concentration of the ester is desirable for dimer formation. The use of a hypodermic syringe and syringe pump is most advantageous for this purpose since the rate of addition can be very precisely controlled.

Dimer formation was favored also by using less surface area of sodium in the reaction. The reaction setup was modified to use magnetic stirring instead of a high speed stirrer. The sodium was in the form of spheres $^1/_2$" to $^1/_{16}$" in diameter and the ester was added to the reaction

mixture, at room temperature, in one portion. The reaction mixture then was heated to reflux while being stirred magnetically. This approach gave the silyl-acyloin acids in high yield. However, this approach did not work when short chain (C_6 and C_7) esters were involved because the reaction becomes uncontrollably exothermic.

c. Cyclopropanation of the Silyl-Acyloin Dimer

The cyclopropanation of the silyl-acyloin dimer was conducted using diethylzinc and methlyene iodide rather than the more traditional zinc-copper or zinc-silver couple and methylene iodide. Since diethylzinc is pyrophoric the reaction vessel must be freed of oxygen and moisture and maintained under an inert atmosphere of nitrogen. The silyl-acyloin dimer, diethylzinc, and solvent are stirred under nitrogen, and methylene iodide is added dropwise, producing a mildly exothermic reaction. The addition of diethylzinc to a mixture of unsaturated compound and methylene iodide should be avoided since the reaction sometimes occurs explosively.

Diethylcadmium can be used in place of diethylzinc in this method. The cadmium methylene-transfer reagent behaves very similarly to the corresponding zinc reagent. Thus far, no synthetic advantages have been demonstrated using this variation.

The workup procedure calls for the addition of the reaction mixture to a large volume of saturated aqueous ammonium chloride solution. This serves to destroy any unreacted diethylzinc which remains in the reaction

mixture. This process brings about the formation of zinc oxide which is rather insoluble and causes the formation of an emulsion. Under more acidic conditions the zinc oxide is soluble and an emulsion is not formed; however, the cyclopropanation product undergoes ring opening when the acidity of the solution becomes too great and renders this remedy impractical. It is possible, with difficulty to extract the emulsion with chloroform and recover the cyclopropanation product in this manner. Another drawback to the workup procedure is that any unreacted olefin is hydrolyzed and possibly some of the cyclopropanation product is destroyed as well.

d. Ferric Chloride Oxidation of the Dimeric Cyclopropanation Product

The ferric chloride oxidation of the cyclopropanated dimer was conducted in the same manner as that of the cyclopropanated monomer which was discussed previously. The only difference observed for the dimer was that on a number of occasions the ferric chloride reaction resulted in the formation of a polymer and no ketone could be isolated. This was very possibly due to the formation of coordination complexes from siloxycyclopropanes and the organozinc intermediate of the cyclopropanation reaction, which can be somewhat difficult to hydrolyze and, when present only in traces, may cause

polymerization. The polymers proved to be insoluble in any of the common organic solvents or concentrated HCl and were not characterized.

The acid workup of the reaction mixture containing the tetraketones was done in the same manner as that of the reaction mixtures containing diketones. The removal of iron from the chloroform extract was incomplete even with 50% (50 mL concentrated HCl diluted to 100 mL) HCl treatment.

B. THE CHELATES OF THE MACROCYCLIC-1,3-DIKETONES

1. Trends in Chelation

A survey of the chelating abilities of the 1,3-diketones, produced in this study, was conducted and the results of this survey are given in Table III. Only the chelation results for the C_{10}, C_{11} and C_{13} macrocyclic 1,3-diketones are given in Table III, because the C_7 and C_9 macrocycles did not form chelates with any of the metals studied. Obviously the larger the macrocycle the less specific it becomes with respect to chelation.

The extractibilities of the chelates formed in this study were determined for five solvents of various polarity. The solvents were methylisopropyl ketone (3-methyl-2-butanone) (MIK), chloroform (Chl), benzene (Bz), diethyl ether (DEE), and tri-n-butyl phosphate (TBP). The results of this survey appear in Table IV. The chelates seemed to extract into each of these

TABLE III

Chelation Survey of The Macrocyclic-1,3-Diketones With Various Common Metal Ions

Metal Ion	Macrocyclic-1,3-Diketones Surveyed				
	C_7	C_9	C_{10}	C_{11}	C_{13}
Be(II)	NR	NR	NR	NR	NR
Mg(II)	NR	NR	NR	NR	white ppt
Al(III)	NR	NR	NR	NR	NR
Cr(III)	NR	NR	NR	NR	NR
Mn(II)	NR	NR	NR	NR	white ppt
Fe(III)	NR	NR	red ppt	red ppt	red ppt
Co(II)	NR	NR	NR	pink ppt	pink ppt
Ni(II)	NR	NR	NR	green ppt	green ppt
Cu(II)	NR	NR	blue ppt	blue ppt	blue ppt
Zn(II)	NR	NR	NR	NR	white ppt
Pd(II)	NR	NR	NR	NR	yellow ppt
Cd(II)	NR	NR	NR	NR	white ppt

TABLE IV

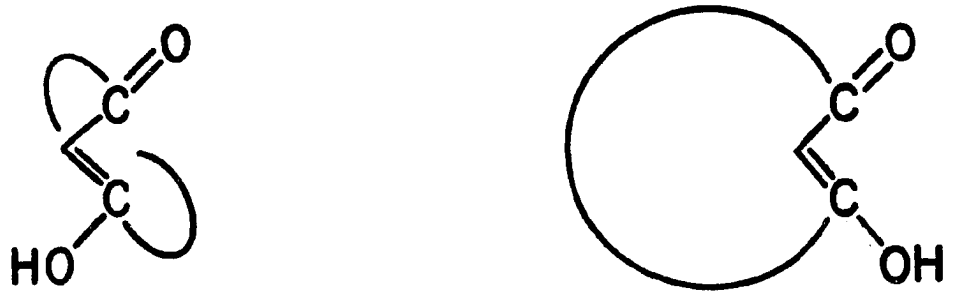
Extraction Survey of The
Macrocyclic-1,3-Diketone Chelates Prepared in This Study

Chelate	MIK	Chl	Bz	DEE	TBP
C_{10}-Fe	0	+	0	0	+
C_{10}-Cu	0	+	0	0	+
C_{11}-Fe	0	+	0	0	+
C_{11}-Co	+	+	+	+	+
C_{11}-Ni	+	+	+	+	+
C_{11}-Cu	0	+	0	0	+
C_{11}-Pd	+	+	+	+	+
C_{13}-Mg	+	+	+	+	+
C_{13}-Mn	+	+	+	+	+
C_{13}-Fe	0	+	0	0	+
C_{13}-Co	+	+	+	+	+
C_{13}-Ni	+	+	+	+	+
C_{13}-Cu	0	+	0	0	+
C_{13}-Zn	+	+	+	+	+
C_{13}-Pd	+	+	+	+	+
C_{13}-Cd	+	+	+	+	+

Legend: + = chelate dissolved in extractant
0 = chelate extracted but some undissolved chelate remained in extractant
MIK = Methylisopropyl ketone
Chl = Chloroform
Bz = Benzene
DEE = Diethyl Ether
TBP = Tri-n-Butyl Phosphate

solvents with the best extraction taking place with chloroform and tri-n-butyl phosphate.

It was not surprising to find that the seven member cyclic ketone did not chelate with any of the metals since trans enolization is disallowed in rings with less than eight members. It was somewhat surprising to find that the nine member ketone did not form chelates with any of the metals. The lack of chelation in these smaller cyclic ketones is thought to be due to a lack of enolization at all rather than the wrong orientation, i.e., cis vs. trans enolization.



cis trans

2. Degree of Enolization of the Macrocyclic-1,3-Diketones

The degree of enolization of the macrocyclic-1, 3-diketones in $CDCl_3$ at 300°K was established by consideration of the 200 MHz proton nmr spectra of these compounds under the conditions given. Table V gives the results of this analysis. The relative amount of keto form to enol form was derived by taking the height of the keto peak and two times the height of the enol peak (these

peaks are due to the protons on the carbon positioned between the oxygen bearing carbons) respectively and dividing by the sum of the keto peak height and two times the enol peak height. The relative amounts of keto and enol forms of acetylacetone under the same conditions are provided in Table V for comparison. The effect of ring size on the degree of enolization is obvious and this lack of enolization in the smaller ringed compounds is probably the reason for the greater selectivity in chelation and eventual lack of chelation as the ring size decreases.

The effect of ring size is also present in the chemical shifts of the keto and enol peaks of the macrocyclic-1,3-diketones. These chemical shifts are listed along with those of acetylacetone in Table VI. As the strain in the compound increases the absorptions of the keto and enol protons both move upfield.

3. Volatility Characteristics of the Chelates

The thermal stability of the chelates is in the general order $C_{10}<C_{11}<C_{13}$, with the copper chelates being the most thermally stable of the metals studied. In most cases only decomposition occurred and in the other instances sublimation was accompanied by decompositon of varying degrees. The twenty and twenty-two carbon tetraketone copper chelates proved to be less volatile than the corresponding ten and eleven carbon diketone copper chelates. This is illustrated in Figure 8 which is the

TABLE V

Degree Of Enolization Of The Macrocyclic-1,3-Diketones

Ketone	Height of Peak (cm)[a] Keto	Enol	% Keto form	% Enol form
Acetyl Acetone	0.3	2.2	6.38	93.62
C_{13}	4.9	7.1	25.65	74.35
C_{11}	24.9	1.2	91.21	8.79
C_{10}	----	---	100.00	0.00
C_9	----	---	100.00	0.00
C_7	----	---	100.00	0.00

a. These peaks are due to the protons on the carbon positioned between the oxygen bearing carbons.

TABLE VI

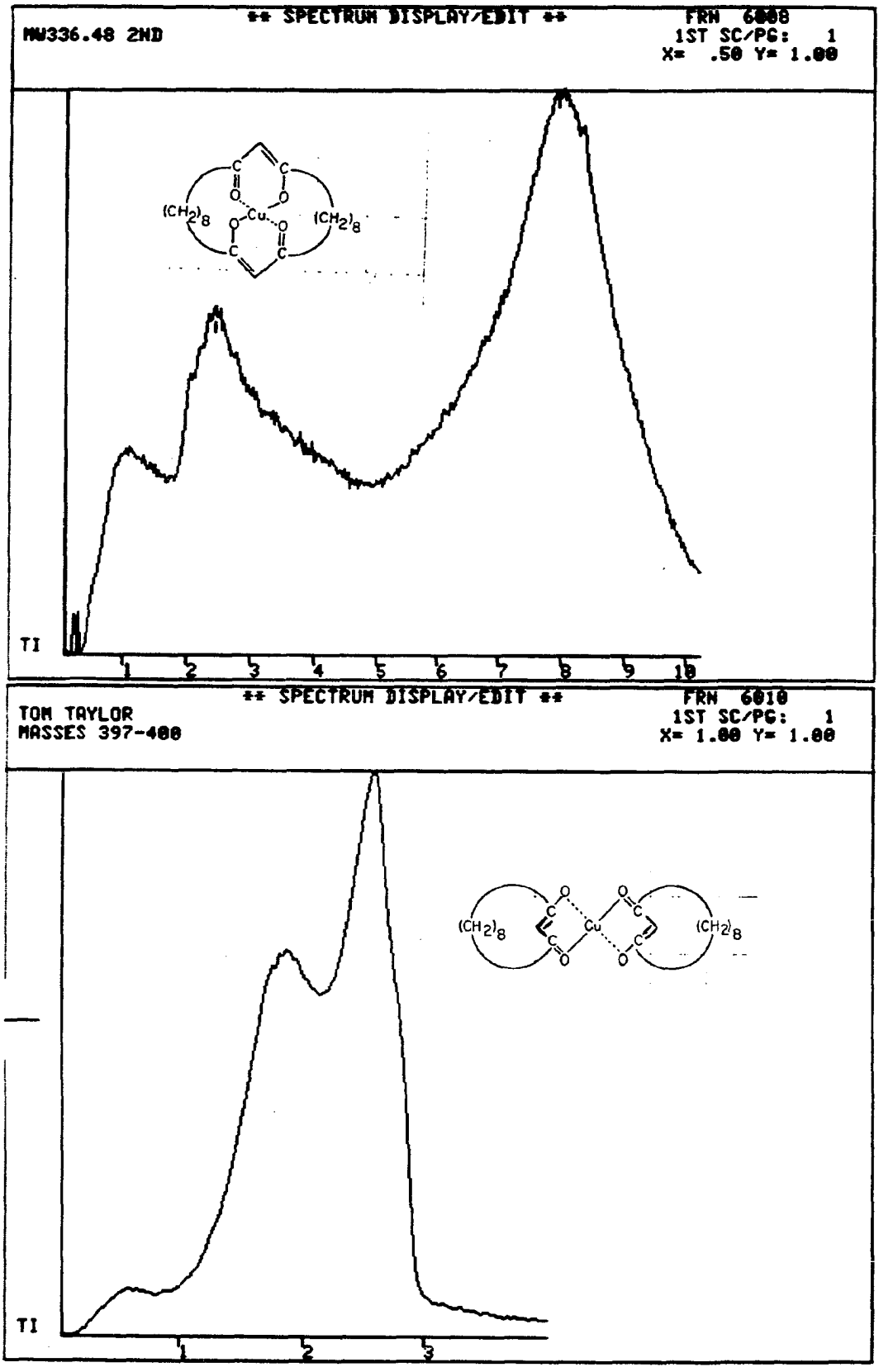
The NMR Chemical Shifts of The Keto and Enol Protons[a] of The Macrocyclic-1,3-Diketones

ligand	Chemical Shift Keto	Enol
Acetyl Acetone	3.500	5.450
C_{13}	3.607	5.704
C_{11}	3.659	5.801
C_{10}	3.663	-----
C_9	3.688	-----
C_7	3.702	-----

a. These protons are those on the carbon positioned between the oxygen bearing carbons.

FIGURE 8

Total Ion Spectra of C_{11}-Diketone Copper Chelate and C_{22}-Tetraketone Copper Chelate



total ion spectra vs. time of the copper chelates of the eleven carbon diketone and the twenty-two carbon tetraketone. The largest peaks in both cases yielded appropriate mass spectra. The probe was temperature programed to start at 30°C and increase at a rate of 30°C/minute. The maxima of the largest peaks coincide with probe temperatures of 105°C and 265°C respectively. The apparent difference in volatility of these two copper chelates is rather surprising. The two chelates have identical molecular weights and the type of bonding is the same for both. It was thought that the tetraketone chelate would exhibit some enhancement of volatility and thermal stability over that of the corresponding diketone chelate since only one molecule of ligand is involved in the former case as opposed to two molecules of ligand in the latter case. However, this presupposes that the cavity of the tetraketone is large enough to accommodate the metal ion without strain and this assumption is based on molecular model studies which may or may not be accurate. As Figure 1 illustrates, the tetraketones may form monomeric chelates or they may form dimers or long chain polymers. Either of the latter two cases would certainly be expected to have much lower volatility than the corresponding diketone chelate. The mass spectrum (Appendix III) of the tetraketone chelates is that expected for the monomeric chelate. This may be due to decomposition of the polymer in the probe or the

monomeric chelate may have been the product all along. At this time not enough information is available to permit a definite conclusion to be drawn.

CHAPTER FOUR

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Five macrocyclic-1,3-diketones were synthesized and characterized. The size of the ring plays an important role in both the ability of the ligand to chelate metals and the volatility and thermal stability of the resulting chelate. Only the ten, eleven and thirteen carbon diketones formed chelates with the trend in selectivity being $C_{10} > C_{11} > C_{13}$. The selectivity of the chelation reaction of the ten carbon diketone may prove to be useful in the analysis of copper and iron. The volatility and thermal stability of the macrocyclic-1,3-diketonates increases with increasing size of the ligand, $C_{10} < C_{11} < C_{13}$. This being the case, it would be very interesting to have the volatility and thermal stability data for even larger macrocyclic-1,3-diketone chelates. Currently an effort is being made within this research group to produce the C_{14} and C_{16} macrocyclic-1,3-diketones. If the chelates of the larger macrocyclic-1,3-diketones prove to be sufficiently volatile and thermally stable, separations and analyses of the metals may be possible by fractional sublimation and gas chromatography.

Studies are presently being conducted in this group

to determine the effect of ring size of the macrocyclic diketones and tetraketones on the chelate bonds by single crystal X-ray diffraction. The information these studies provide will make it possible to establish the nature of the chelate bonds with respect to ring size and whether a monomeric or polymeric chelate is formed with the tetraketones.

Samples of the macrocyclic-1,3-diketones produced in this study have been given to Professor R. V. Nauman. Professor Nauman's group is presently conducting studies of the electronic spectra of the macrocyclic diketones in order to establish the conformation of the carbonyl functionalities in both the excited and ground states.

The properties of the macrocyclic-1,3-diketone chelates other than volatility and thermal stability were neglected in this study, but may prove to have a great deal of analytical significance. The fact that the chelates are soluble in many of the common organic solvents may lead to their use in separating metals by liquid chromatography and counter current extraction of the chelates.

BIBLIOGRAPHY

1. R. W. Moshier and R. R. Sievers, Gas Chromatography of Metal Chelates, Pergamon Press, New York, N.Y. (1965).
2. C. R. Hauser, F. W. Swamer, and J. T. Adams, The Acylation of Ketones to Form β-Diketones and β-Keto Esters, in Organic Reactions, Vol. VIII, edited by R. Adams; John Wiley and Sons, Inc., New York, N.Y. (1954).
3. C. Harris and S. E. Livingston, Bidentate Ligands, in Chelating Agents and Metal Chelates, edited by F. P. Dwyer and D. P. Meller; Academic Press, Inc., New York, N.Y. (1964).
4. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds; John Wiley and Sons, Inc., New York, N.Y. (1963).
5. J. P. Fackler, Metal β-Ketonalate Complexes, in Progress in Inorganic Chemistry, Vol. VII, edited by F. A. Cotton; John Wiley, Inc. Interscience Press, New York, N.Y. (1966).
6. J. P. Collman, in Reactions of Coordinated Ligands, The American Chemical Society, Washington, D.C. (1963).
7. J. Selbin, Chem. Rev., 65, 153 (1965).
8. F. A. Cotton, The Infrared Spectra of Transitional

Metal Complexes, in Modern Coordination Chemistry, edited by T. Lewis and R. G. Wilkins, John Wiley Interscience, New York, N.Y. (1960).

9. L. Orgel, An Introduction to Transition Metal Chemistry, 2nd Ed., John Wiley Methuen, New York, N.Y. (1966).

10. F. R. Hartlage, Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana (1964).

11. E. W. Berg and F. R. Hartlage, Anal. Chim. Acta, 33, 173 (1965).

12. E. W. Berg and F. R. Hartlage, Anal. Chim. Acta, 34, 46 (1966).

13. E. W. Berg and J. J. C. Chiang, Anal. Chim. Acta, 40, 101 (1968).

14. P. C. Uden and D. E. Henderson, Analyst, 102, 889 (1977).

15. D.N. Sokolov, Russ. Chem. Rev., 46 (4), 388 (1977). [Translated from Uspekhi Khimii, 46, 740-749 (1977)].

16. R. E. Sievers and J. E. Sadlowski, Science, 201 (4352), 217 (1978).

17. R. E. Sievers, B. W. Ponder, M. L. Morris and R. W. Moshier, Inorg. Chem., 2, 693 (1963).

18. J. E. Schwarberg, R. W. Moshier and J. G. Walsh, Talanta, 11, 1213 (1964).

19. R. Belcher, R. J. Martin, W. I. Stephen, D. E. Henderson, A. Kamalizad and P. C. Uden, Analyt. Chem., 45, 1197 (1973).

20. R. D. Gillard and G. Wilkinson, J. Chem. Soc., 5885 (1963).

21. H. Venning, W. E. Bachmann and D. M. Wilkinson, Gas Chromat., 5, 248 (1967).

22. W. D. Ross, W. G. Scribner and R. E. Sievers, in Gas Chromatography 1970, edited by R. Stock; Elsevier, Amsterdam (1971), p. 369.

23. W. D. Ross, R. E. Sievers and G. Wheller, Jr., Analyt. Chem., 37, 598 (1965).

24. W. R. Wolf, R. E. Sievers and G. H. Brown, Inorg. Chem., 11, 1995 (1972).

25. R. E. Sievers and K. J. Eisentraut, J. Inorg. Nucl. Chem., 29, 1931 (1967).

26. T. Shigematsu, M. Matsui and K. Utsonomiya, Bull. Inst. Chem. Res. Kyoto Univ., 46, 256 (1968).

27. E. W. Berg and N. M. Herrera, Anal. Chim. Acta, 60, 117 (1972).

28. H. A. Swain and D. G. Karraker, Inorg. Chem., 9, 1766 (1970).

29. K. J. Eisentraut and R. E. Sievers, J. Am. Chem Soc., 87, 5254 (1965).

30. J. E. Sicre, J. T. Dubois, K. J. Eisentraunt and R. E. Sievers, J. Am. Chem. Soc., 91, 3476 (1969).

31. E. W. Berg and J. J. C. Acosta, Anal. Chim. Acta, 40 101 (1968).

32. J. E. Schwarber, R. E. Sievers and R. W. Moshier, Analyt. Chem., 42, 1828 (1970).

33. R. Belcher, A. W. L. Dudeney, W. I. Stephen, J. Inorg. Nucl. Chem., 31, 625 (1969).

34. R. E. Sievers, K. J. Eisentraut and C. S. Springer, Advan. Chem. Ser., 71, 141 (1967).

35. C. J. Adams, Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana (1971).

36. M. M. Coombs and R. P. Houghton, J. Chem. Soc., 5015 (1961).

37. A. H. Alberts and D. J. Cram, J. Am. Chem. Soc., 99, 3880 (1977).

38. I. Tabushi, Y. Kobuke, and T. Nishiya, Tetrahedron Letters, 37, 3515 (1979).

39. Y. Ito, T. Sugaya, M. Nakatsuka, and T. Saegusa, J. Am. Chem. Soc., 99, 8366 (1977).

40. C. Lick and K. Schank, Chem. Ber., 111, 2461 (1978).

41. B. Eistert, F. Haupter, and K. Schank, Justus Liebigs Ann. Chem., 665, 55 (1963).

42. B. Eistert and K. Schank, Tetrahedron Letters, 8, 429 (1964).

43. K. Schank, B. Eistert and J. Felzmann, Chem. Ber., 99, 1414 (1966).

44. H. J. Buysch and S. Hunig, Angew. Chem., 78, 145 (1966).

45. S. Hunig and H. Hoch, Liebigs Ann. Chem., 716, 68 (1968).

46. A. Kirrmann and C. Wakselman, Bull. Soc. Chim. De France, 10, 3766 (1967).

47. A. Stutz and H. Reinshagen, Tetrahedron Letters, 31 2821 (1978).

48. Y. Ito, S. Fujii, and T. Saegusa, J. Org. Chem., 41 2973 (1976).

49. Y. Ito and T. Saegusa, J. Org. Chem., 42, 2326 (1977).

50. S. L. Piekut and W. H. Okamura, Syn. Comm., 10, 415 (1980).

51. H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, Organic Reactions, 20, 1 (1973).

52. J. M. Conia, C. Girard, and J. M. Denis, Synthesis, 1972, 549.

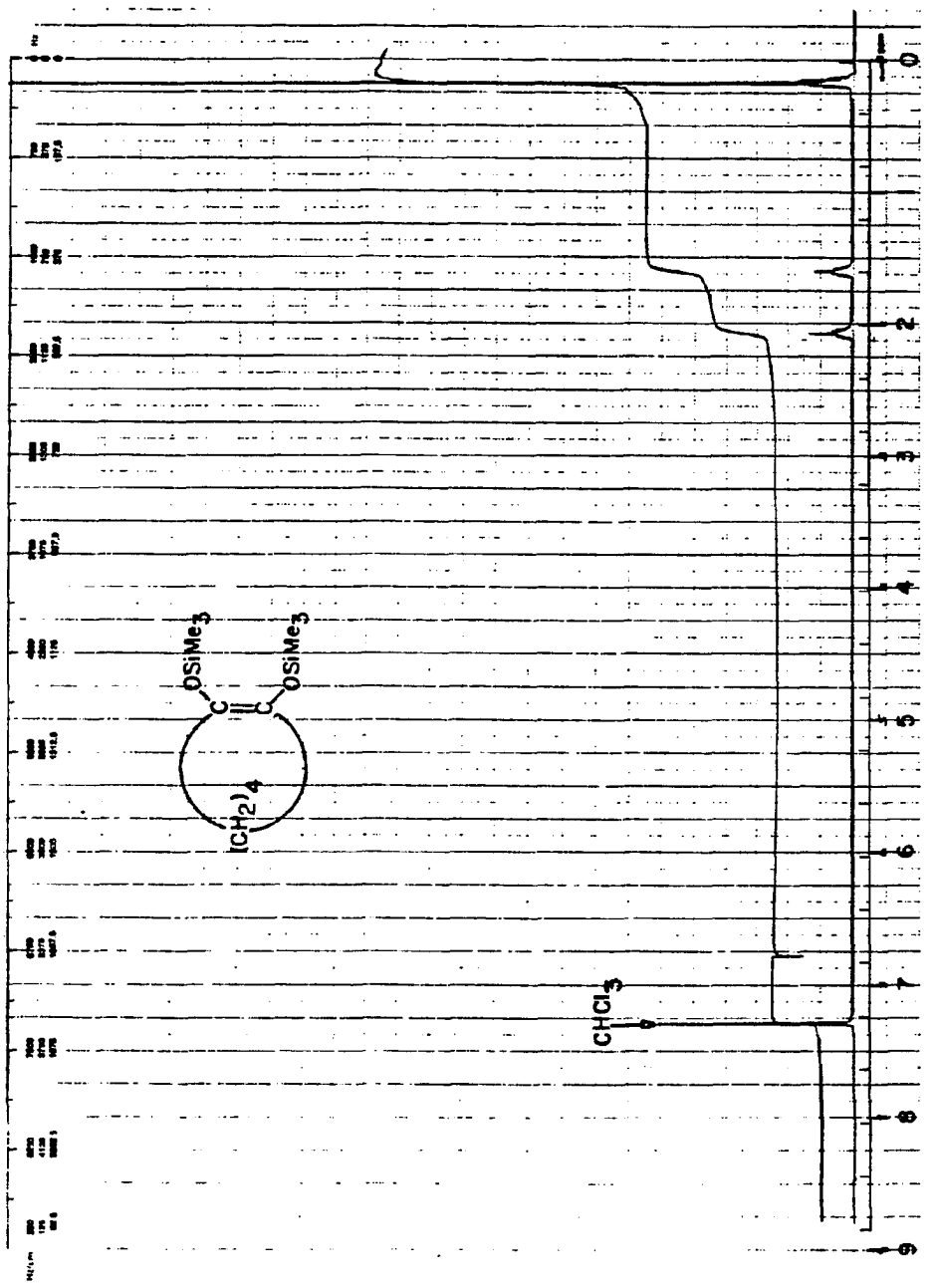
53. K. Ruhlmann, Synthesis, 236 (1971).

54. J. J. Bloomfield, D. C. Owsley, J. M. Nelke, Organic Reactions, 23, 259 (1976).

APPENDIX I

Nuclear Magnetic Resonance Spectra

LIST OF NMR SPECTRA



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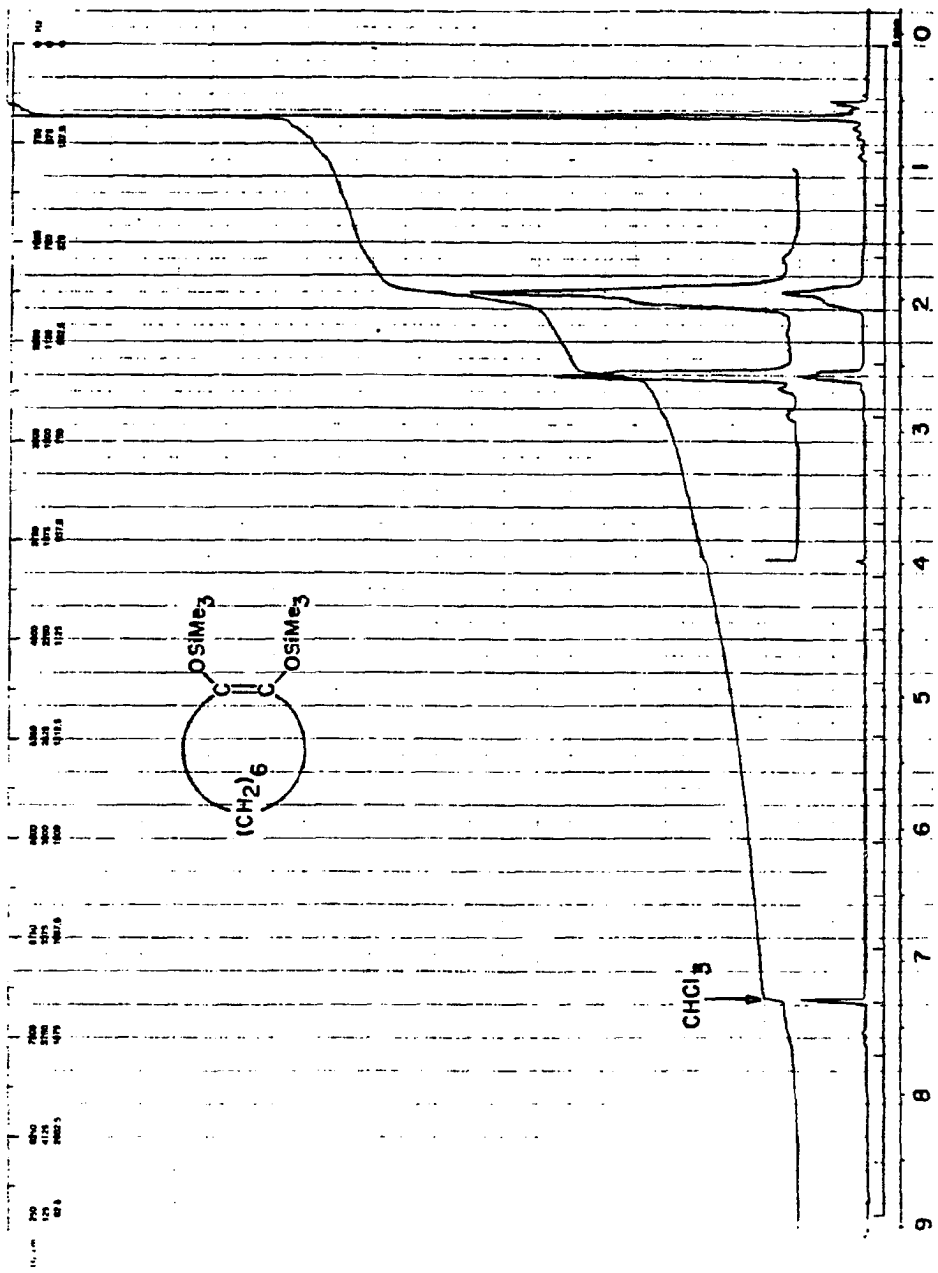

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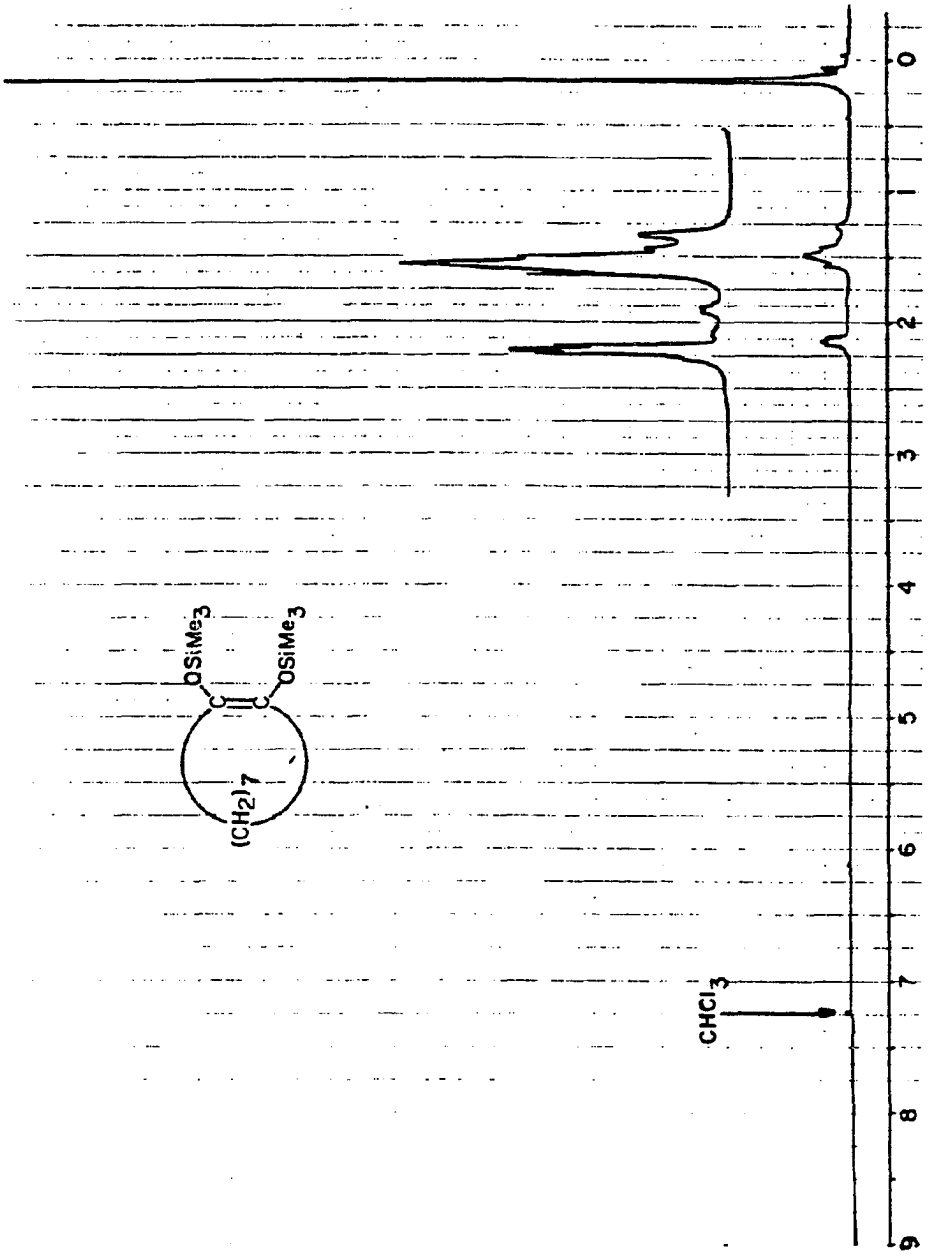

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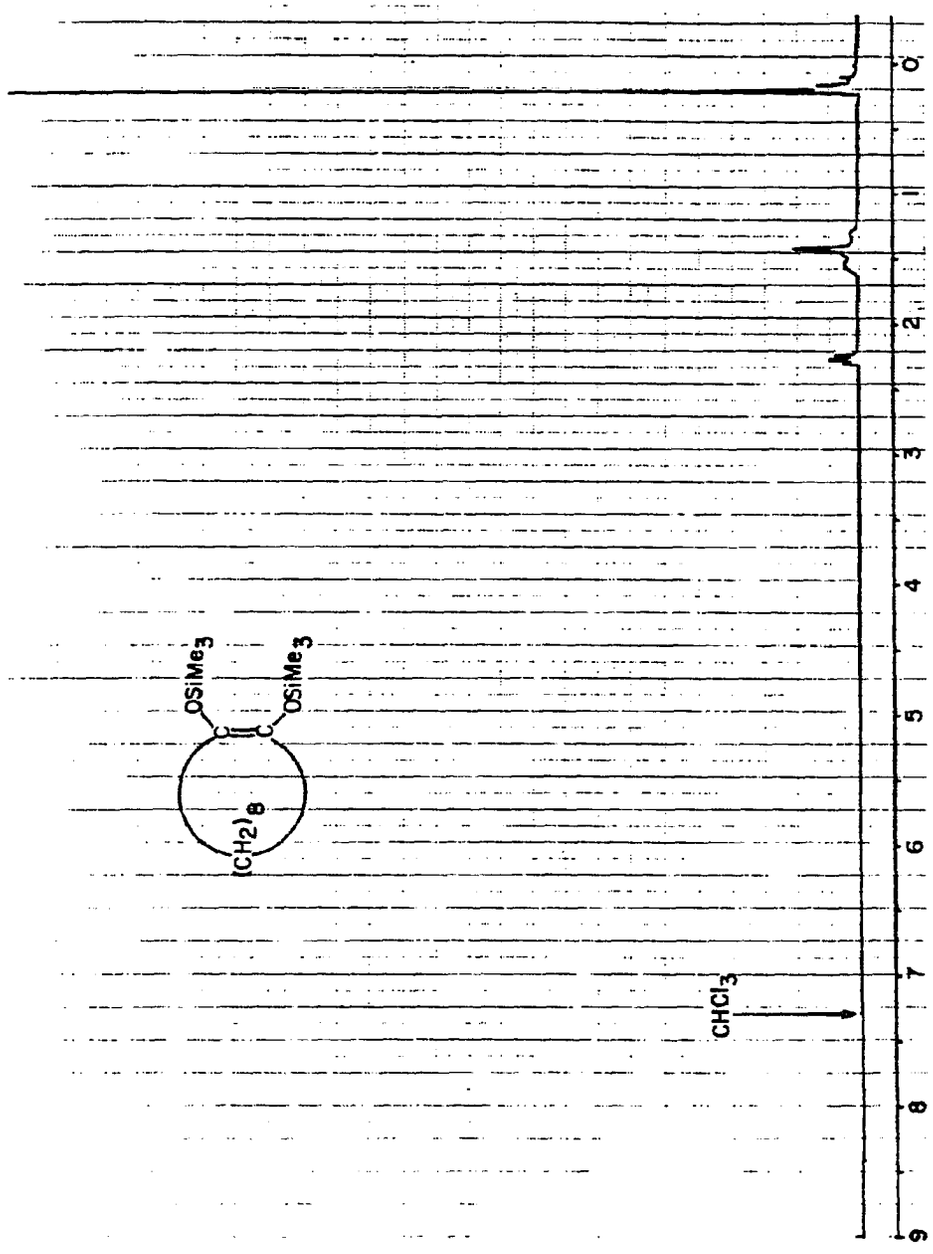

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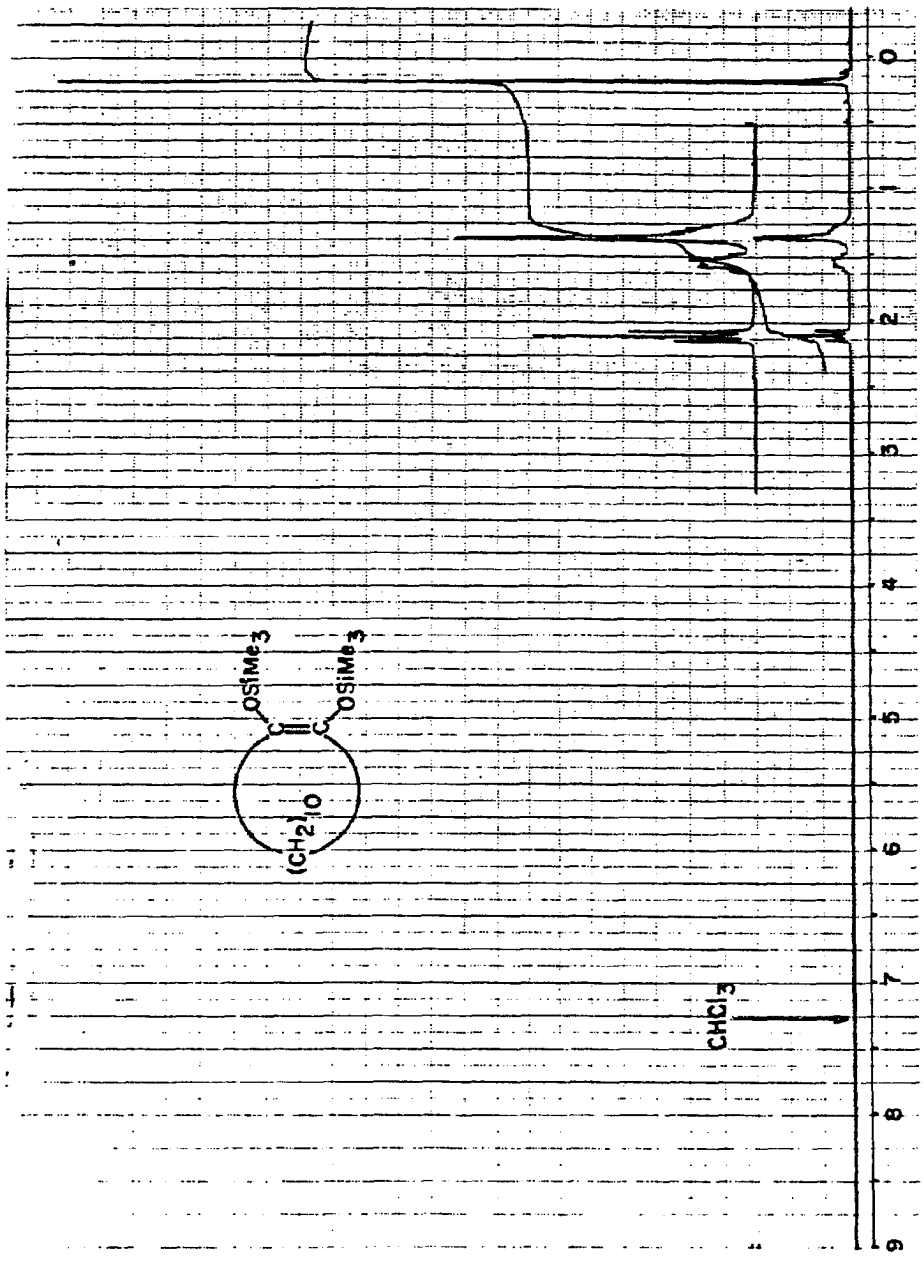

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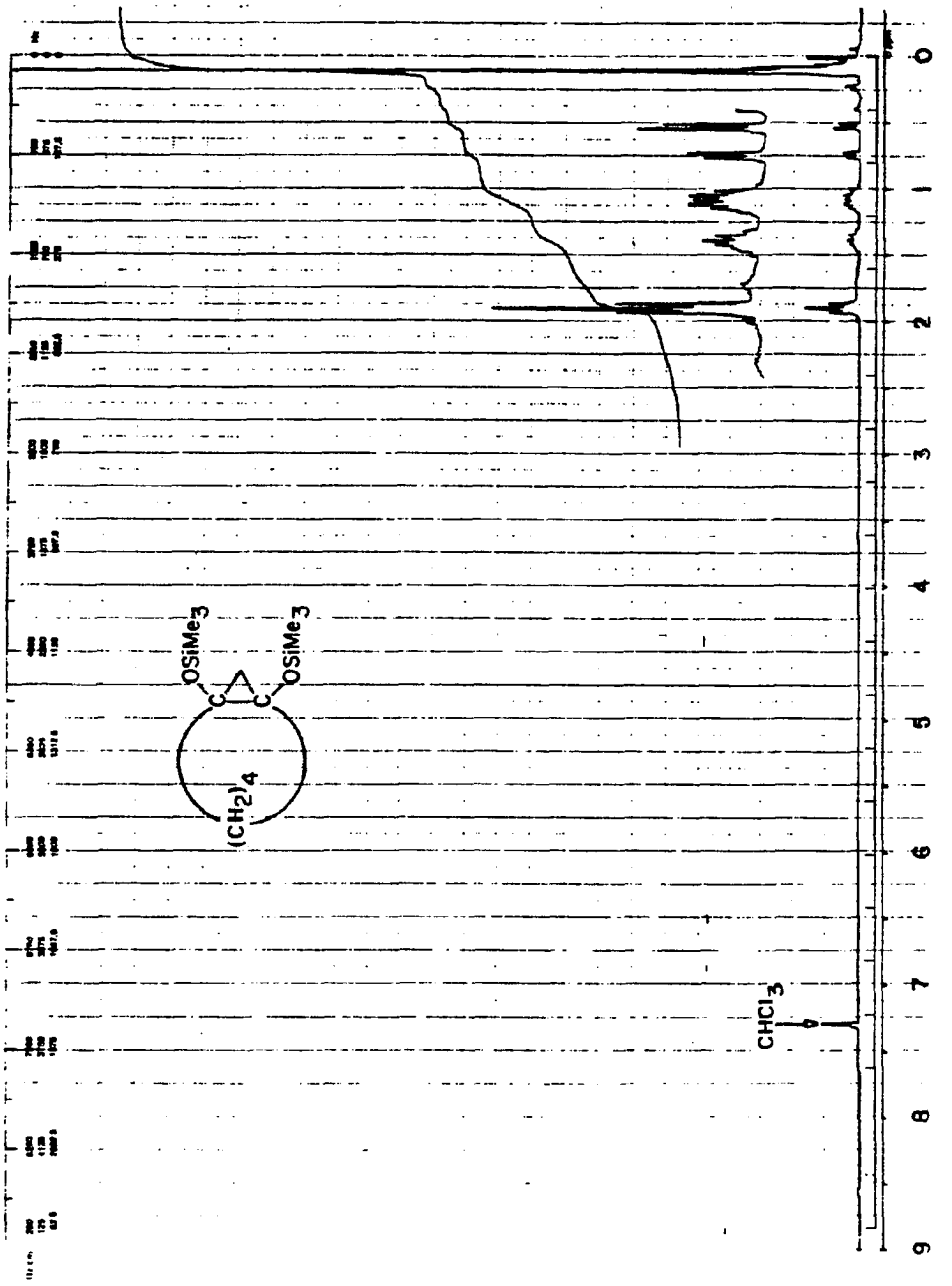

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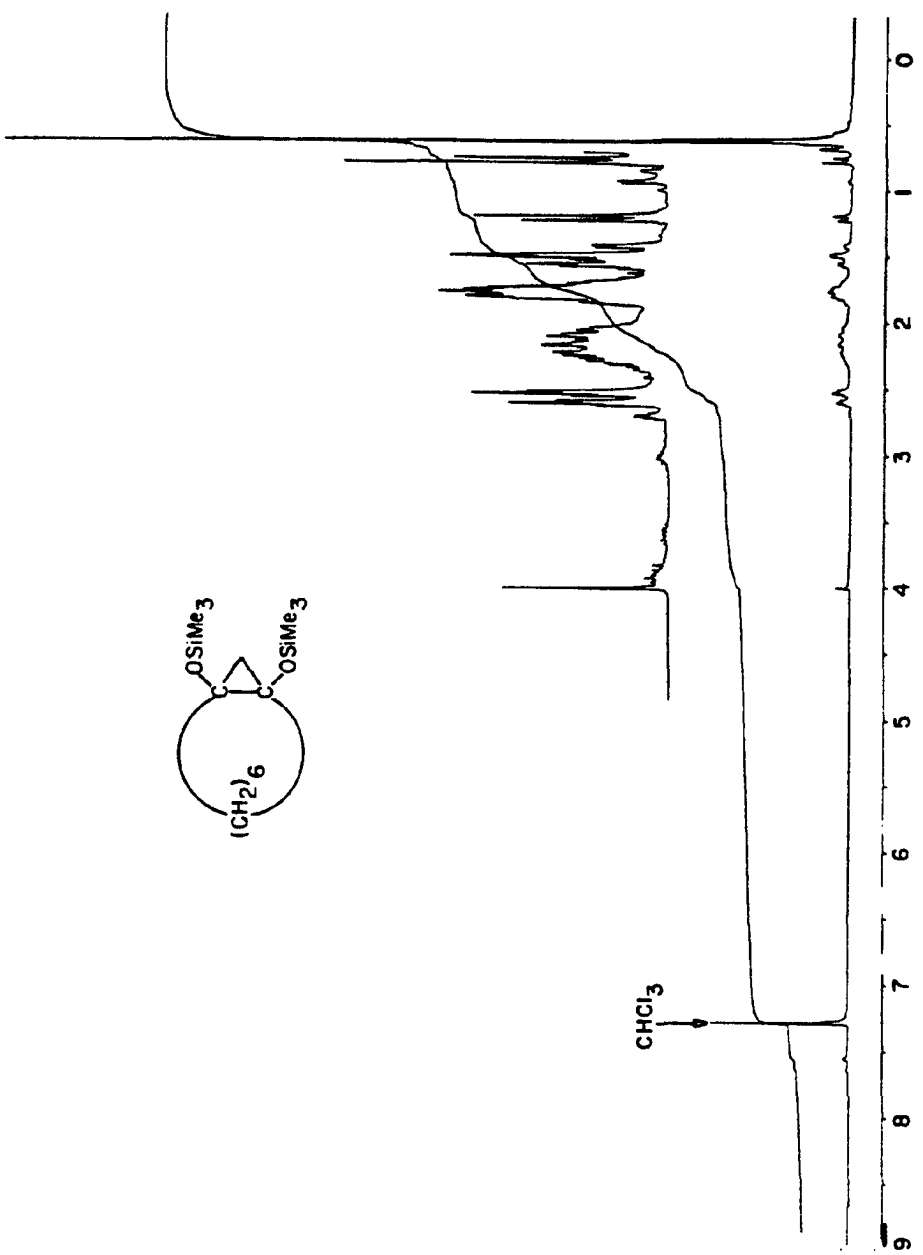

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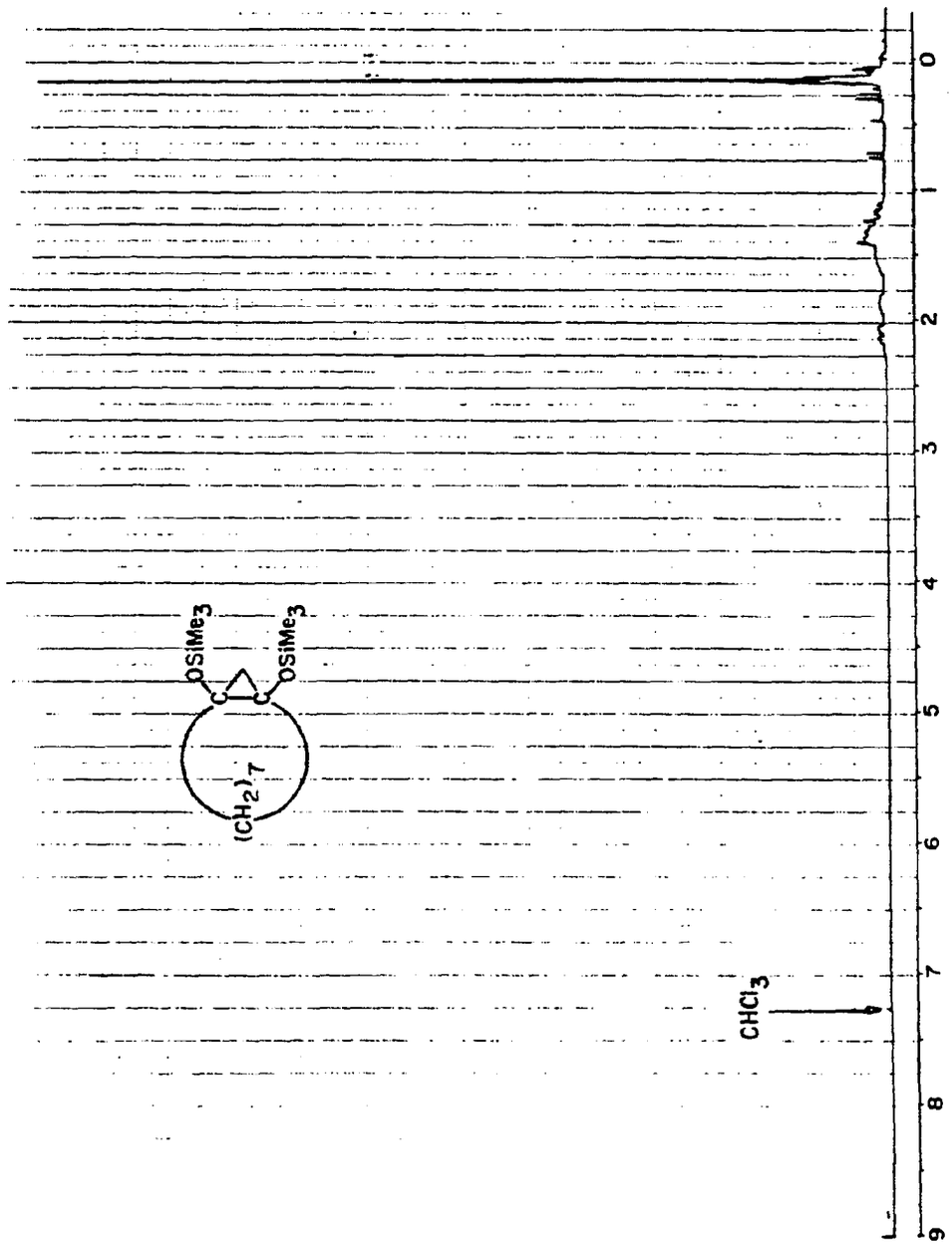

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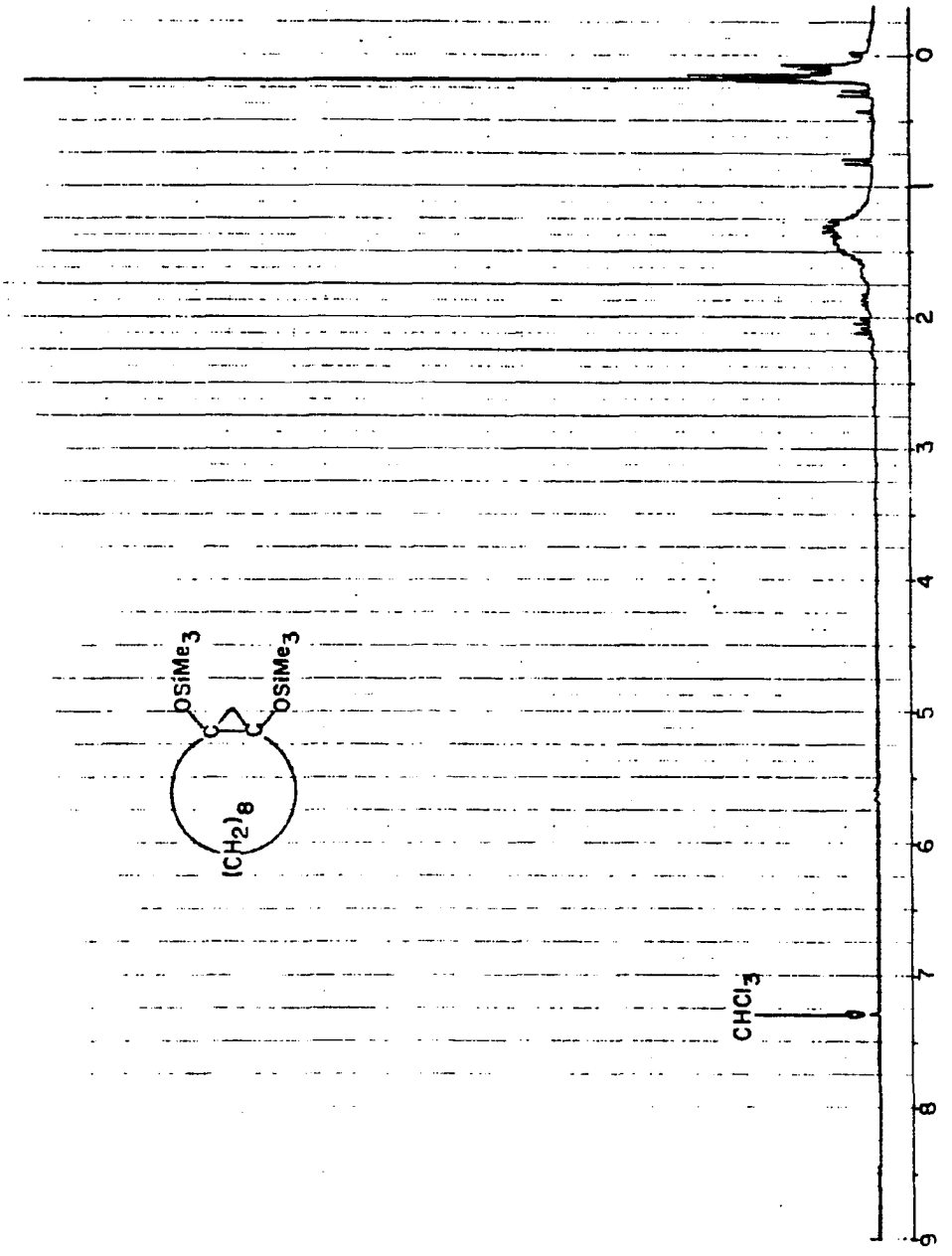

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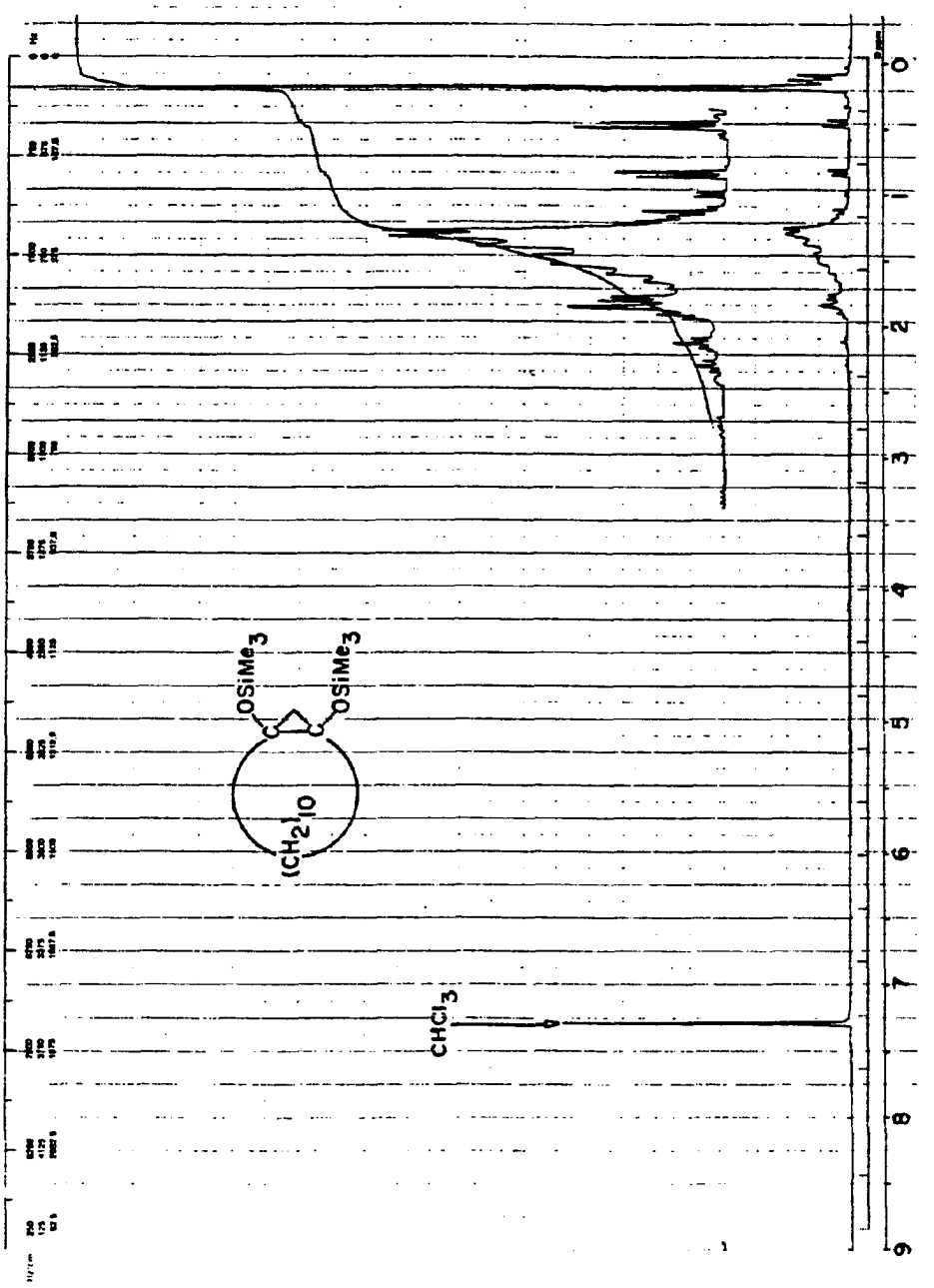

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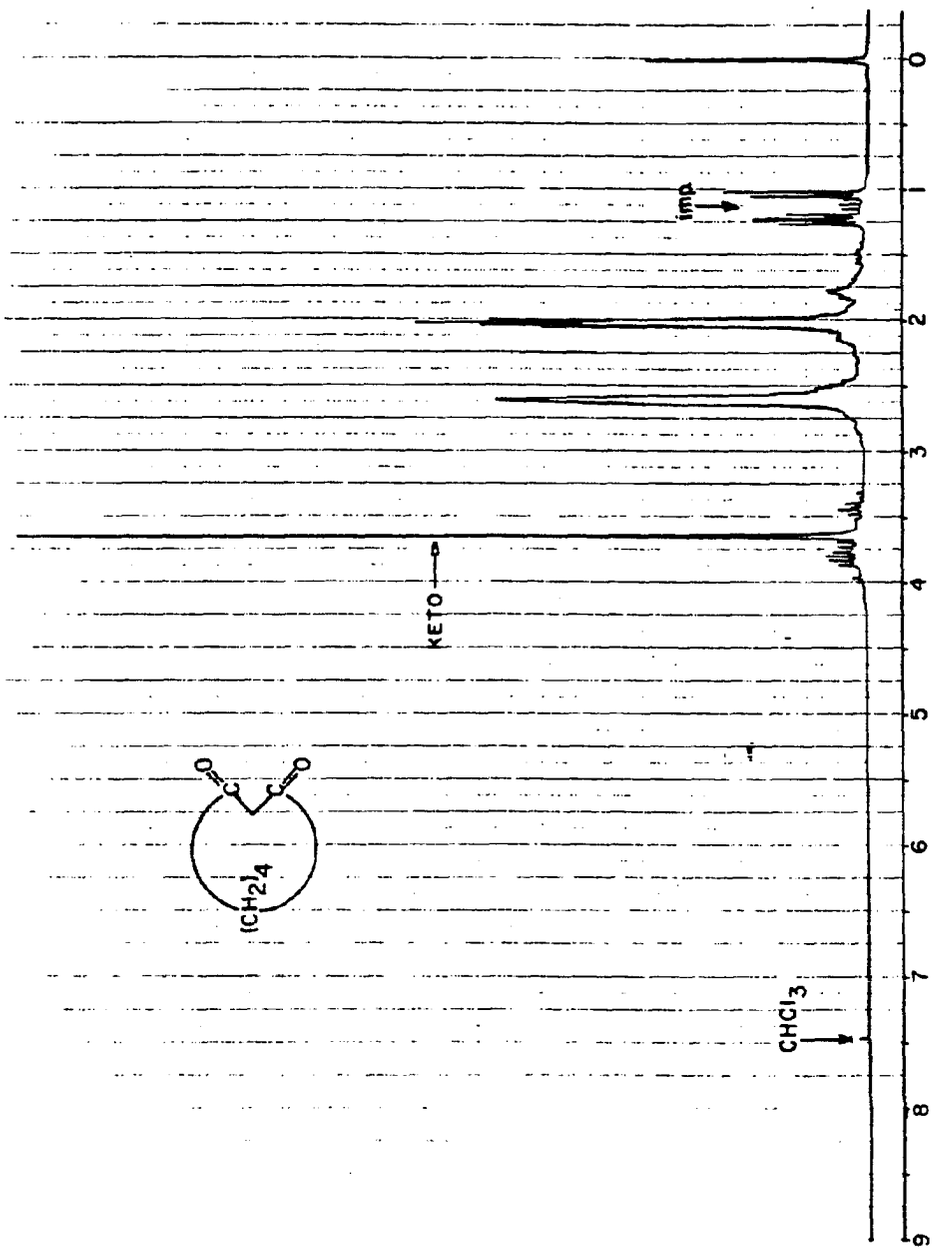
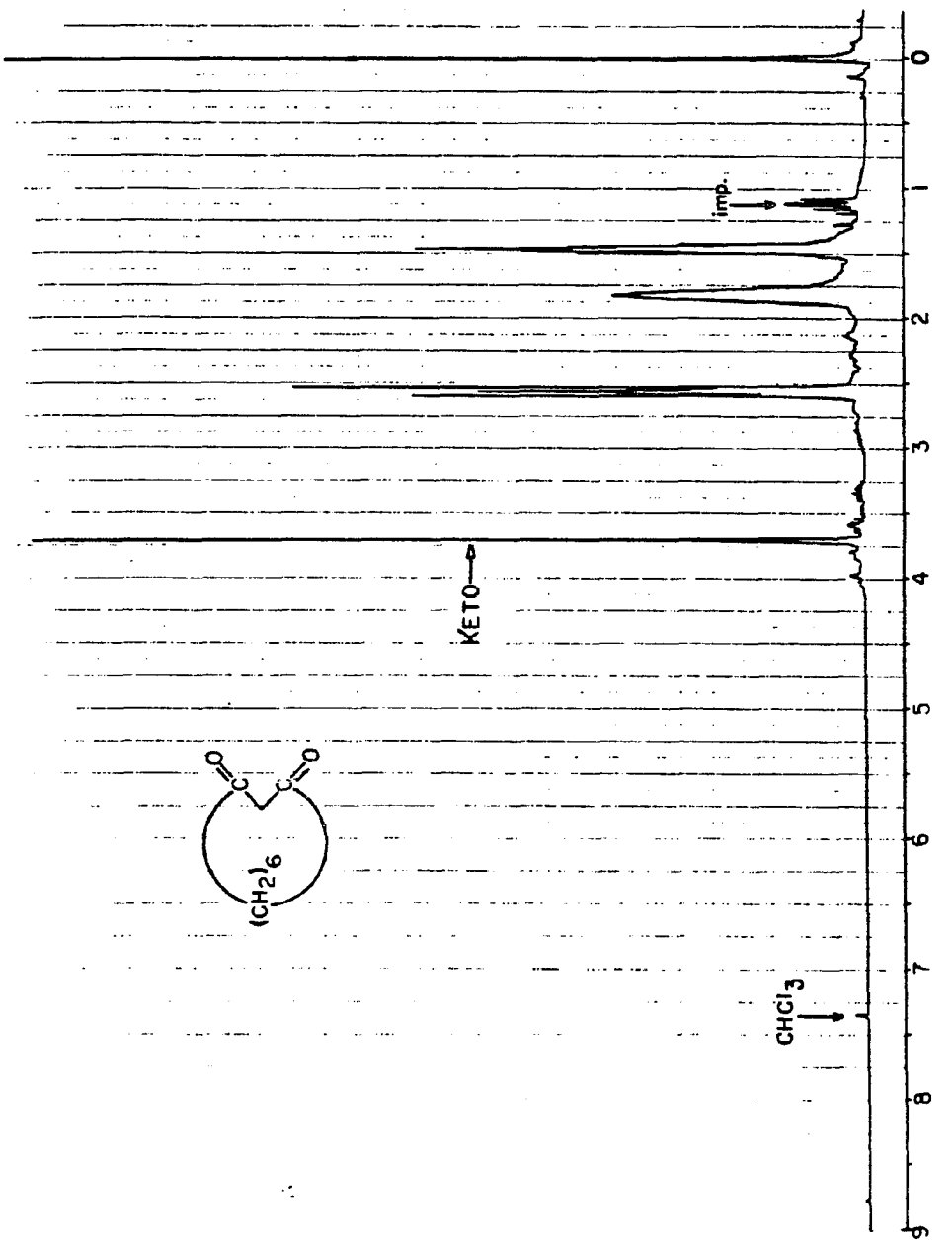


NMR Spectra No. 11

Cycloheptane-1,3-dione



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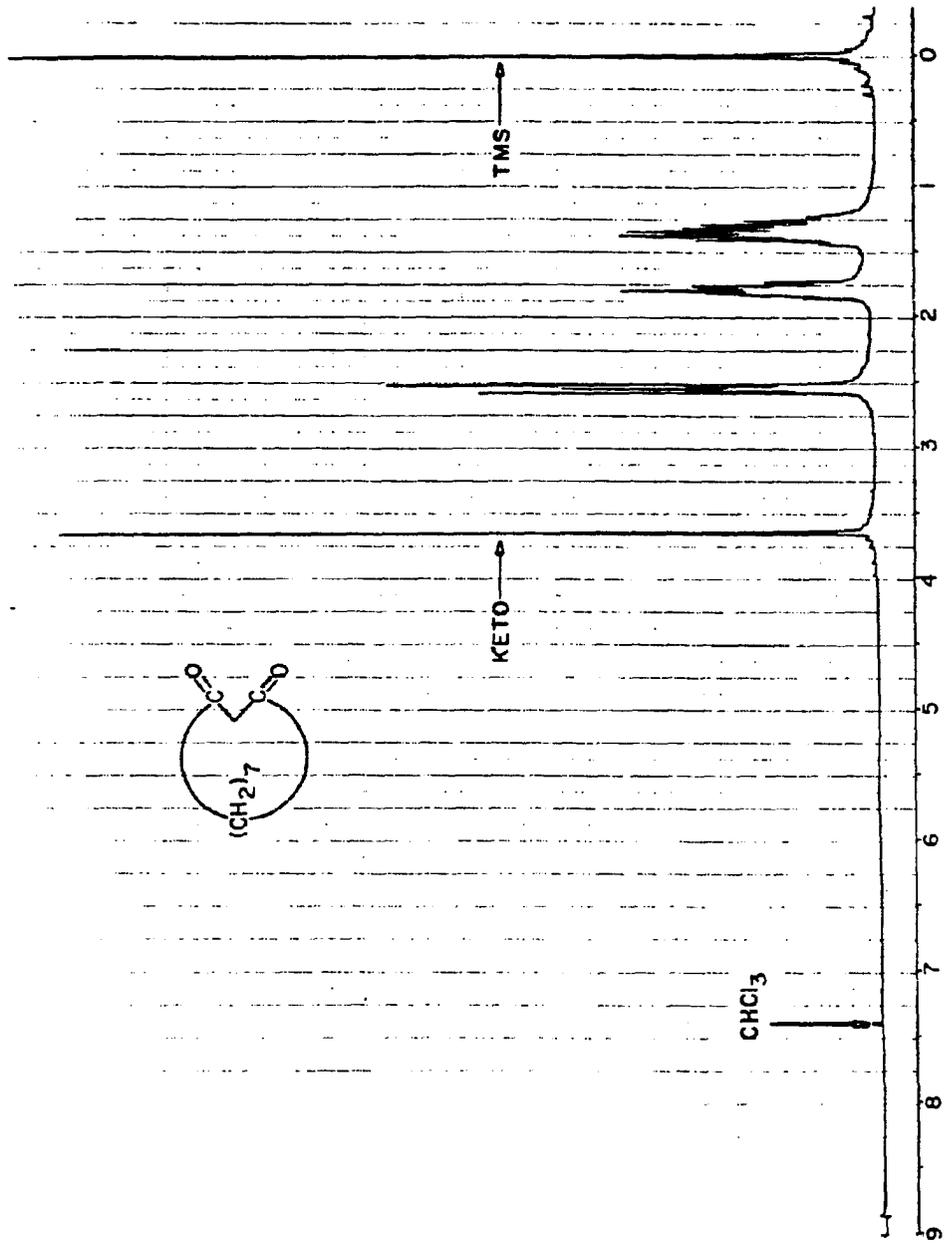

NMR Spectra No. 13

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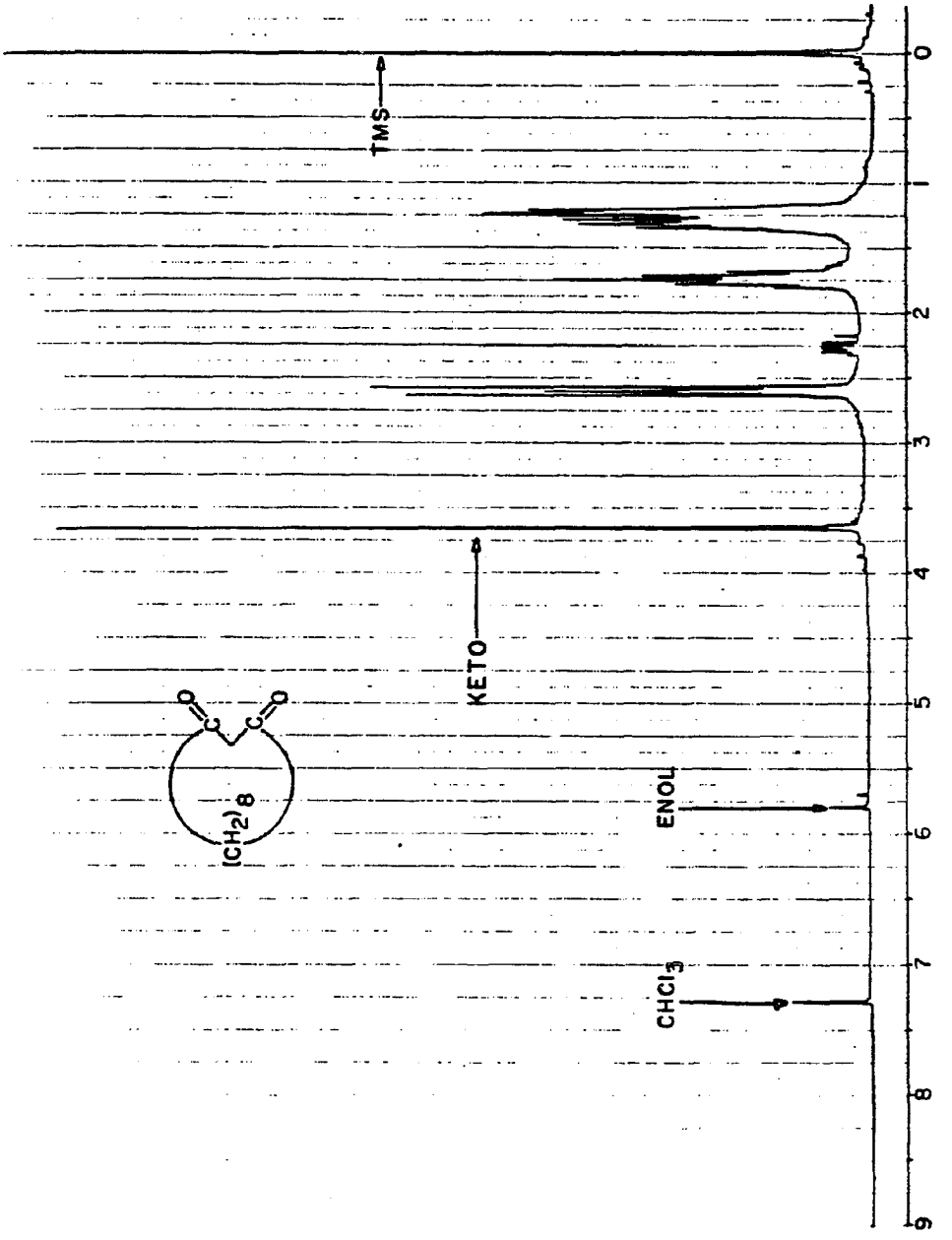

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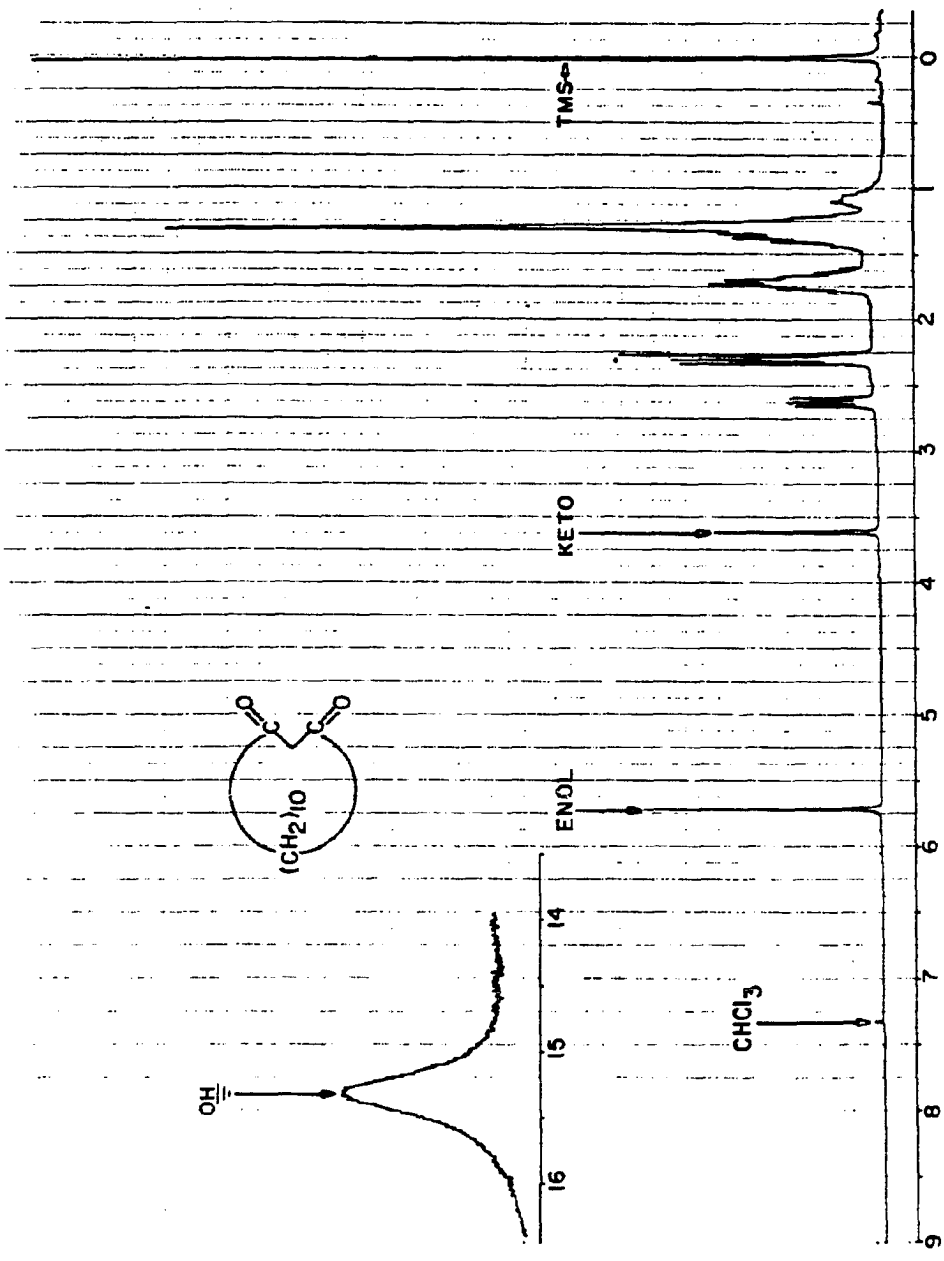


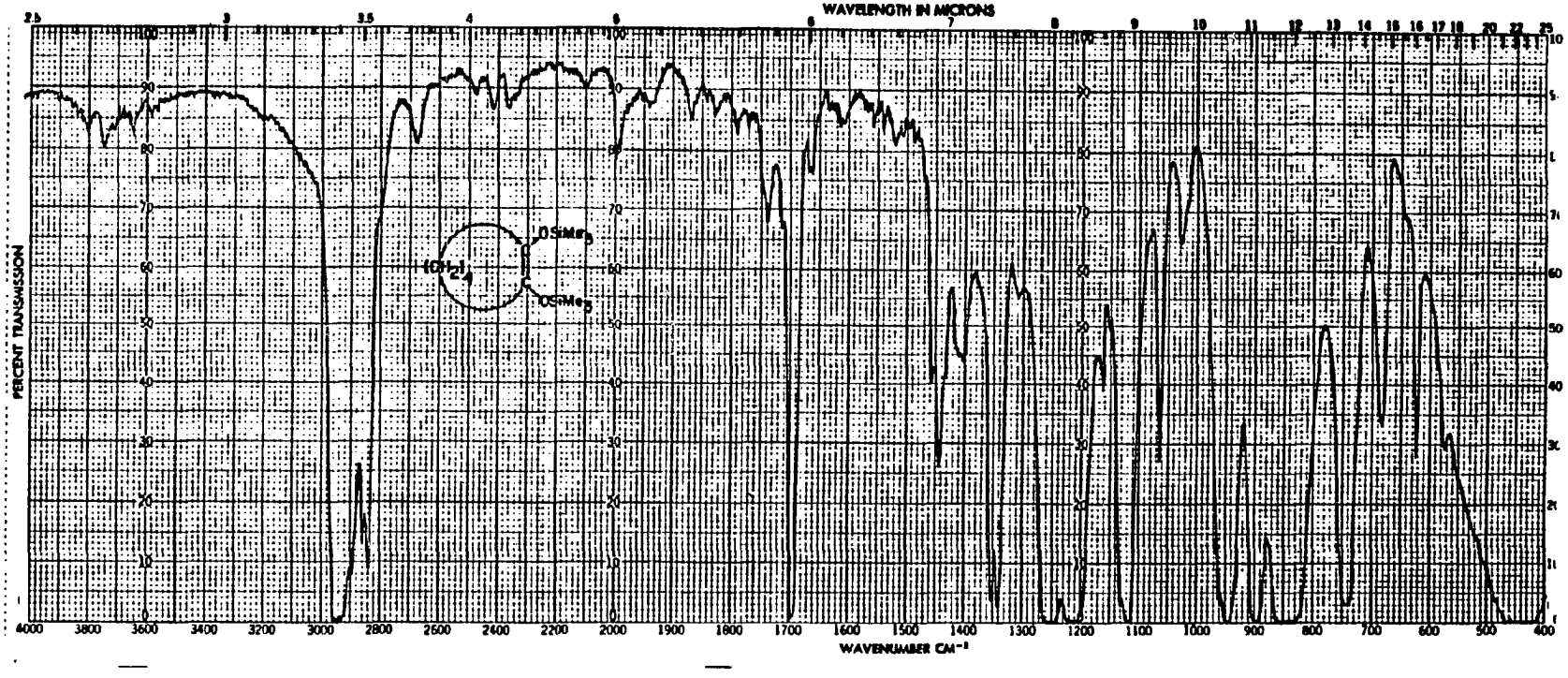
NMR Spectra No. 15

Cyclotridecane-1,3-dione

APPENDIX II

Infrared Spectra

LIST OF INFRARED SPECTRA



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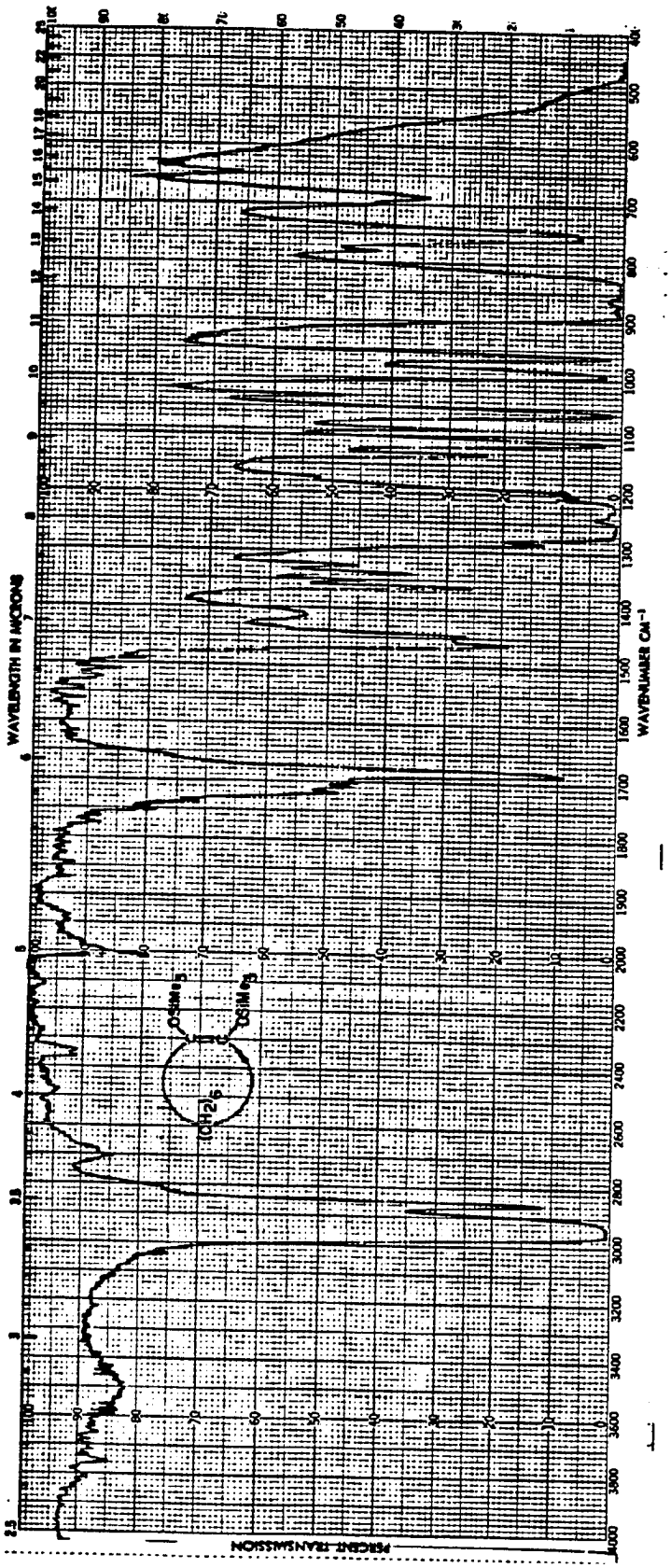

Infrared Spectra No. 2

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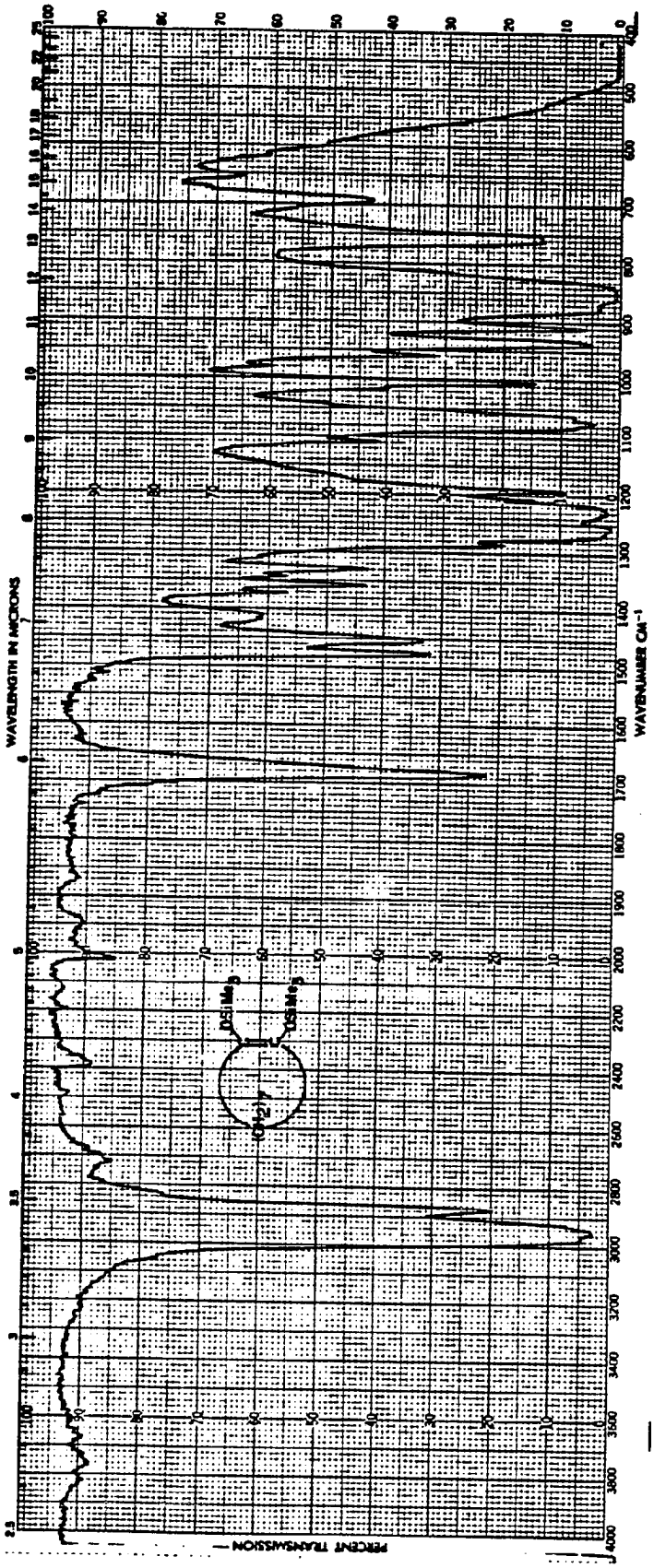

Infrared Spectra No. 3

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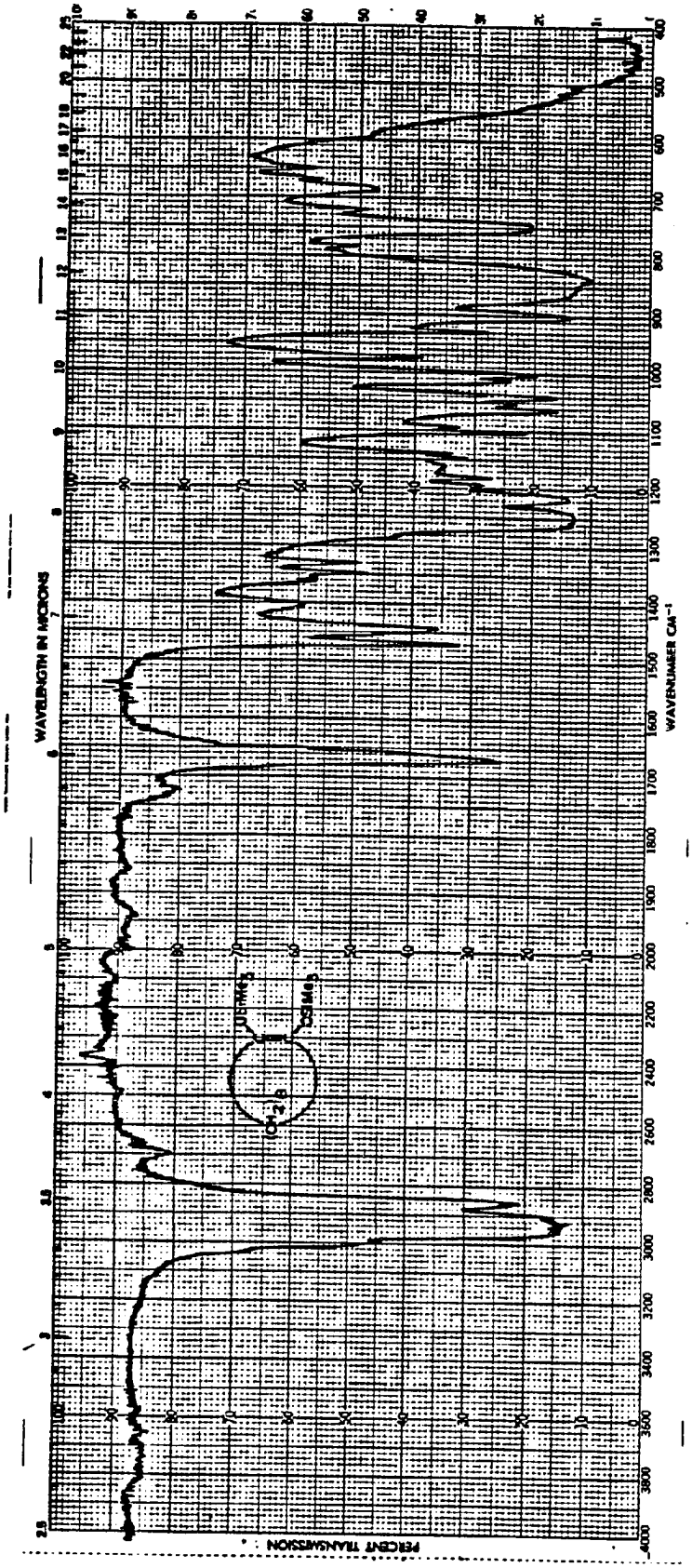

Infrared Spectra No. 4

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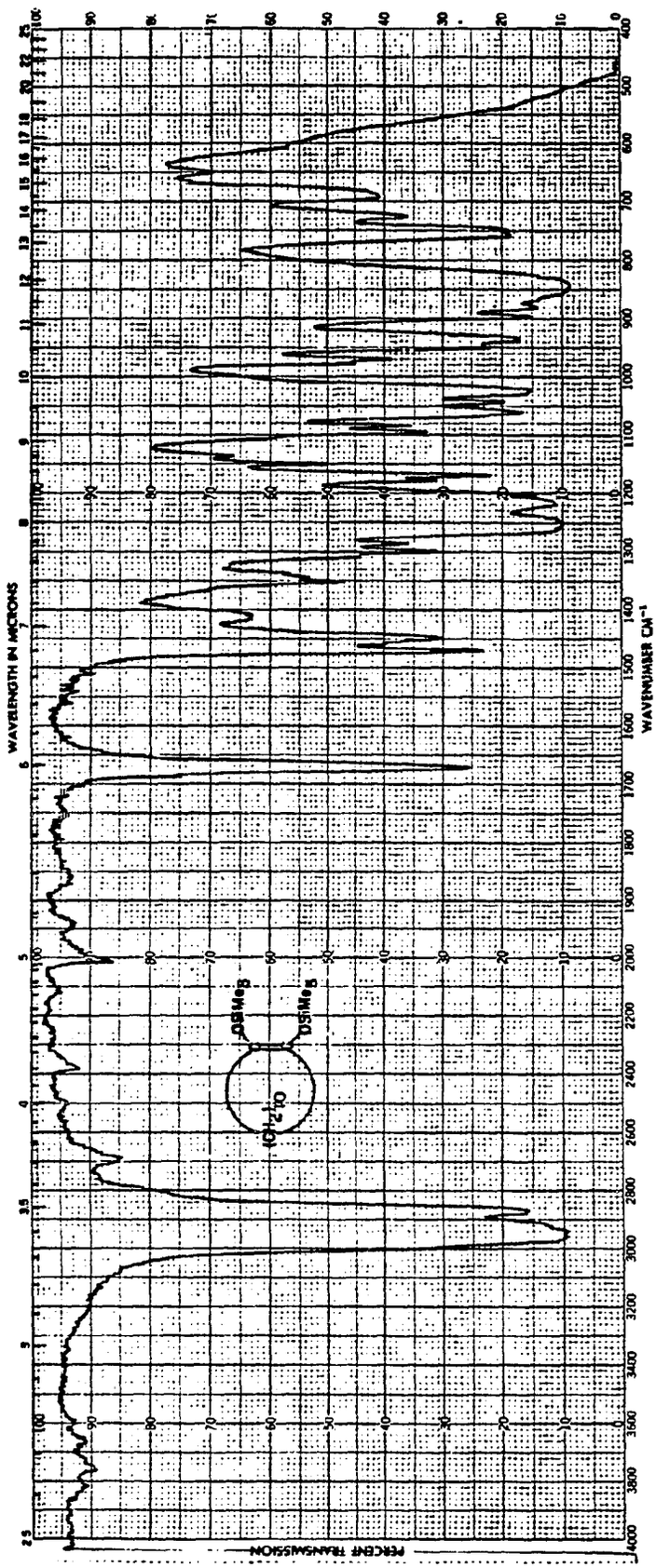

Infrared Spectra No. 5

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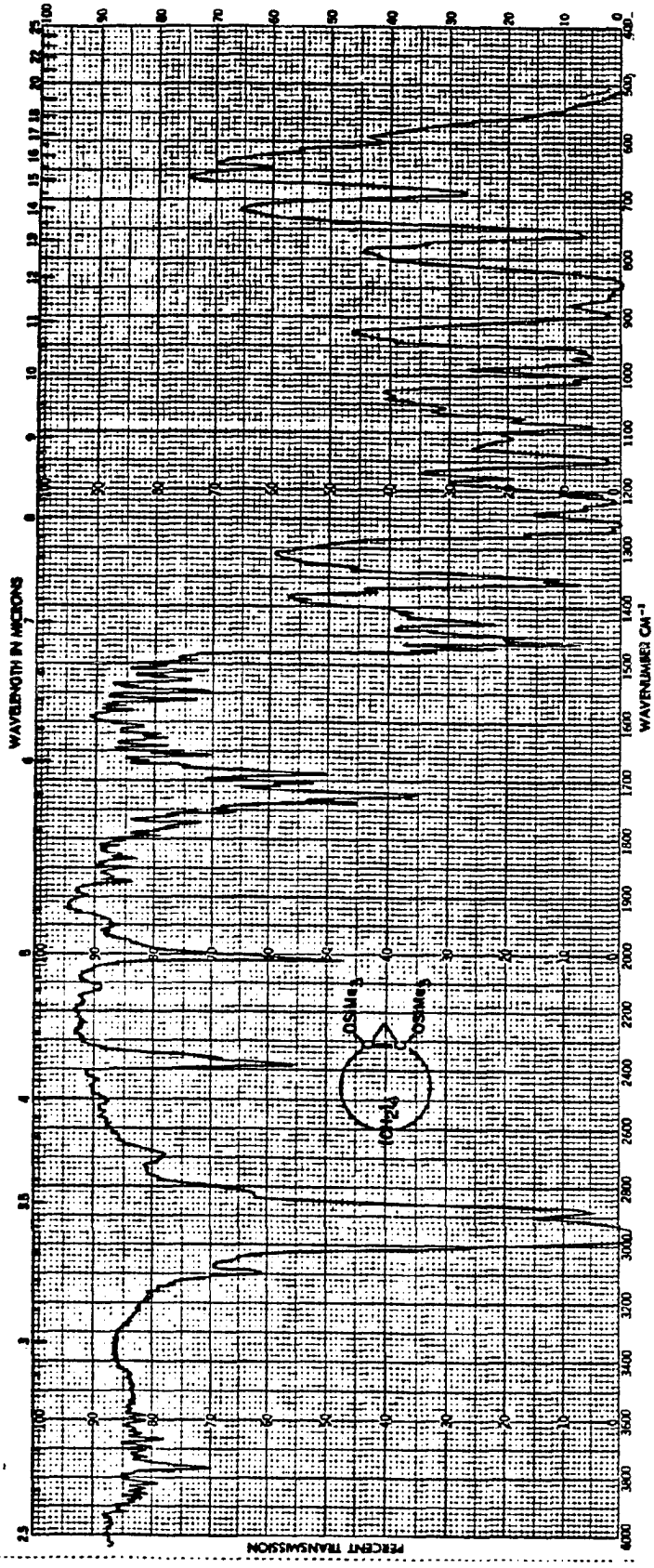
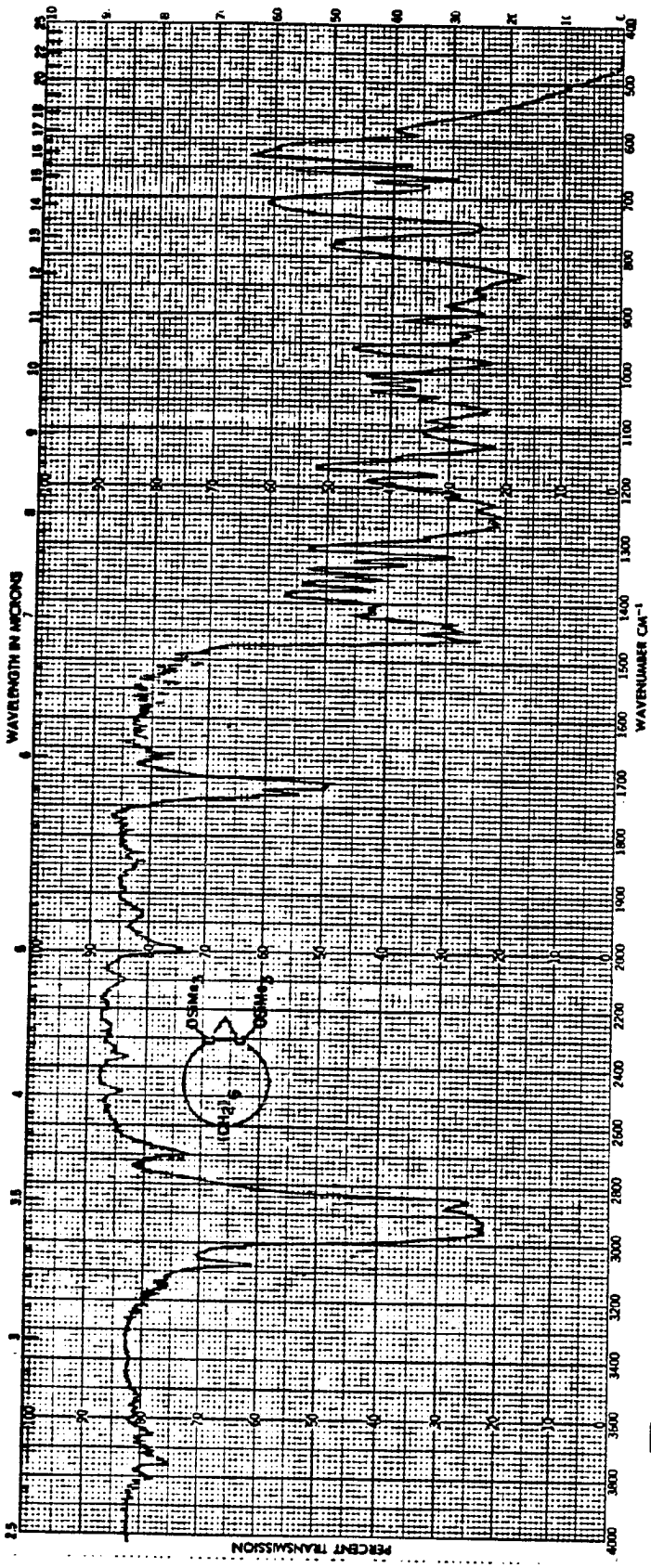


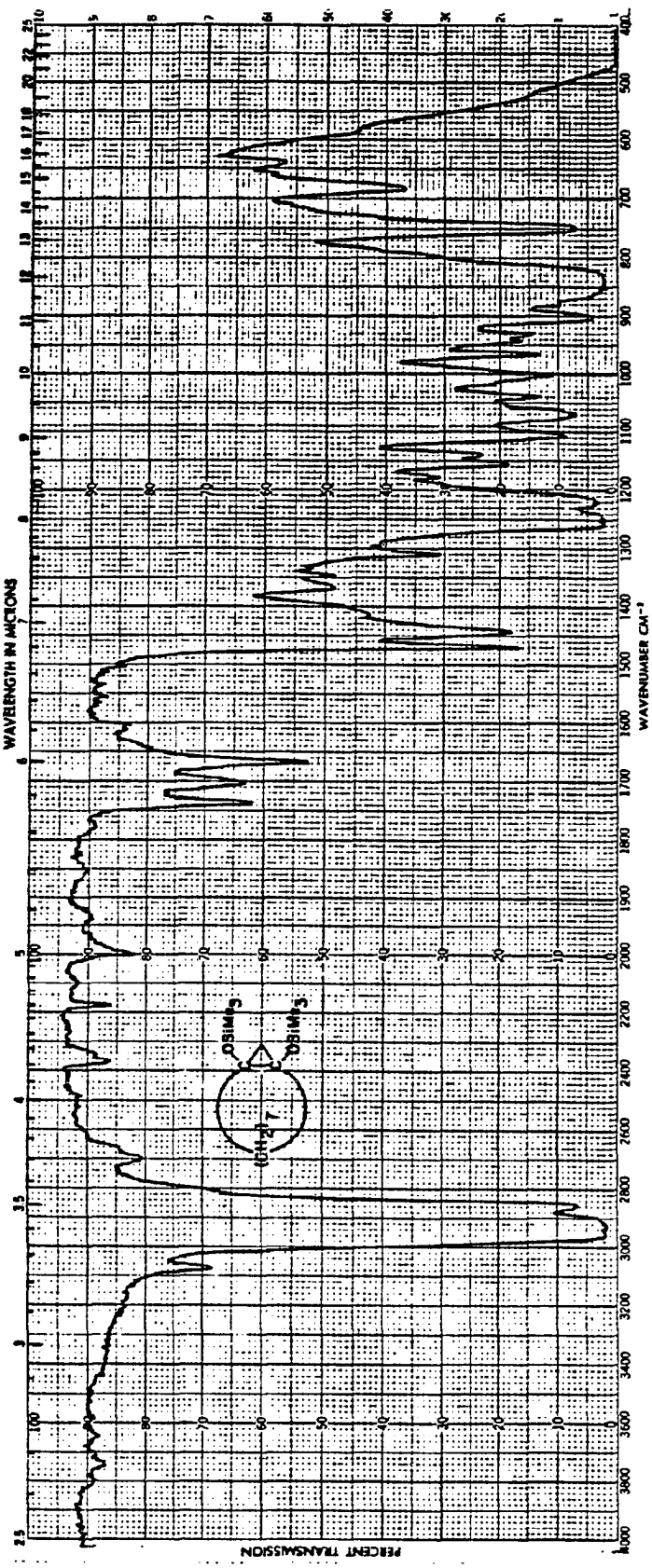
Infrared Spectra No. 6

1,6-Bis(trimethylsilyloxy)bicyclo[4.1.0]



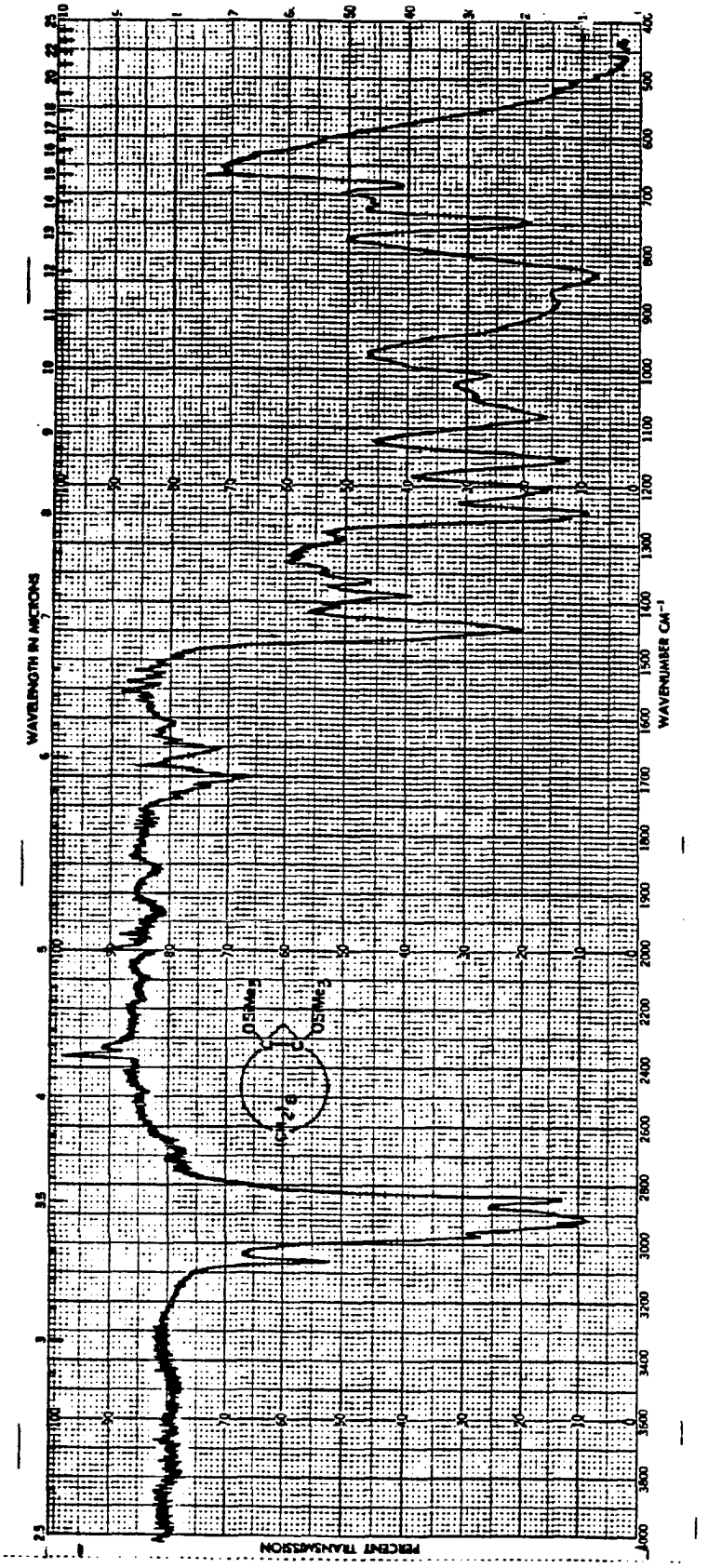
Infrared Spectra No. 7

1,8-Bis(trimethylsilyloxy)bicyclo[6.1.0]nonane



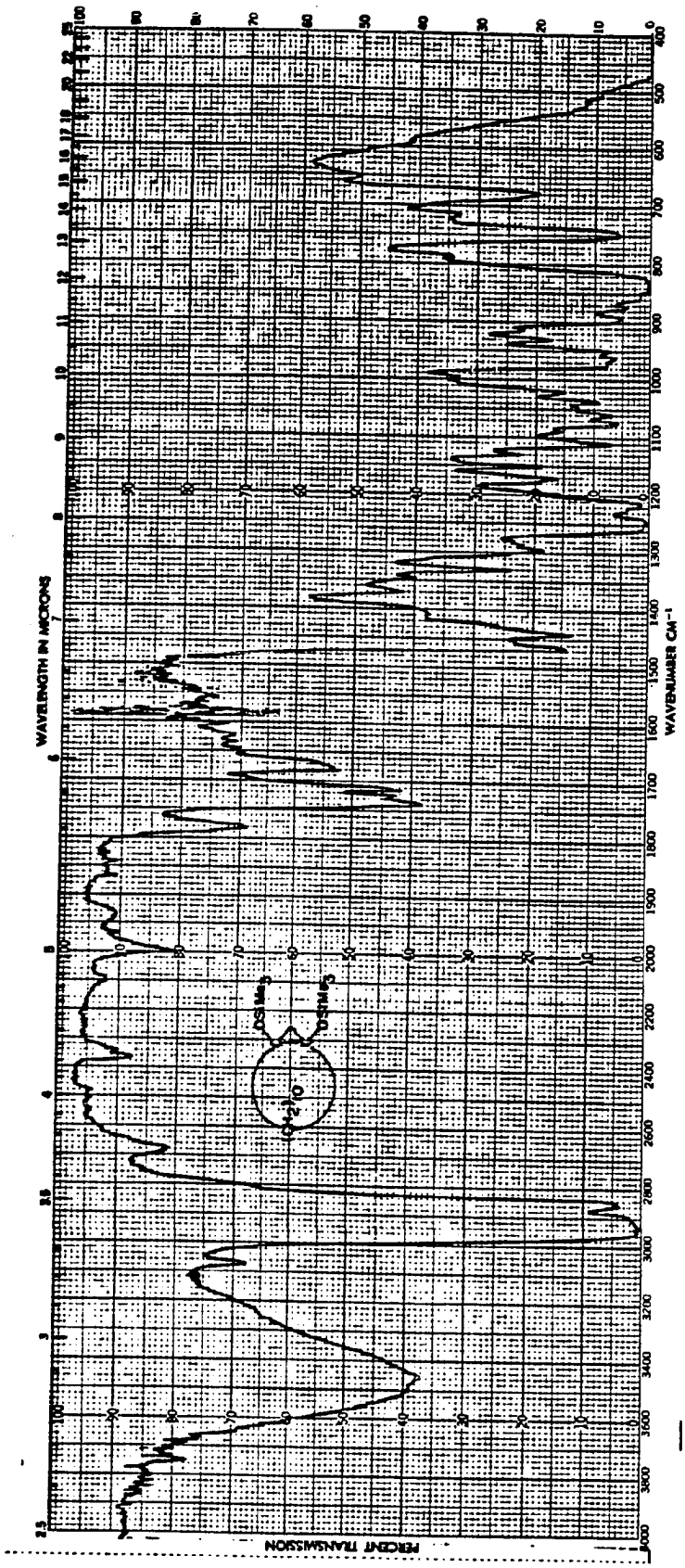
Infrared Spectra No. 8

1,9-Bis(trimethylsilyloxy)bicyclo[7.1.0]decane



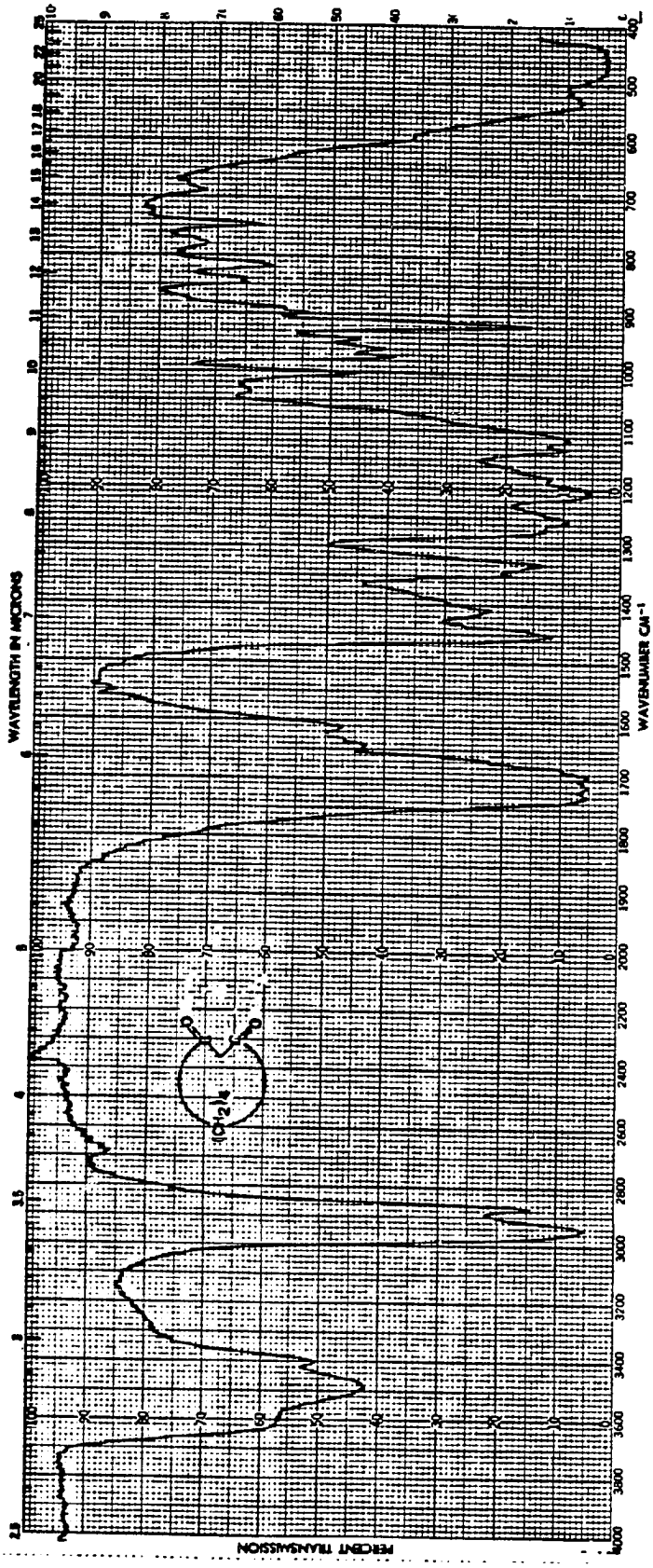
Infrared Spectra No. 9

1,10-Bis(trimethylsilyloxy)bicyclo[8.1.0]undecane



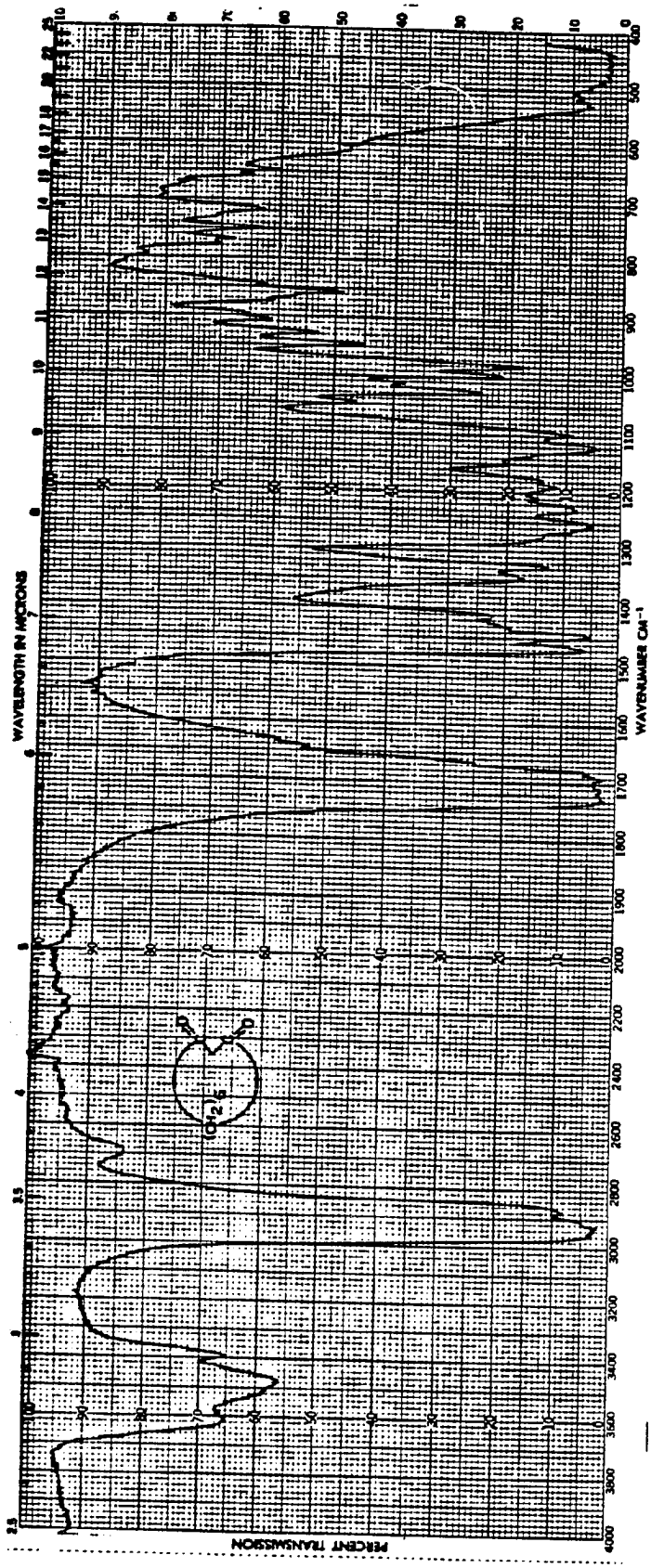
Infrared Spectra No. 10

1,12-Bis(trimethylsilyloxy)bicyclo[10.1.0]tridecane



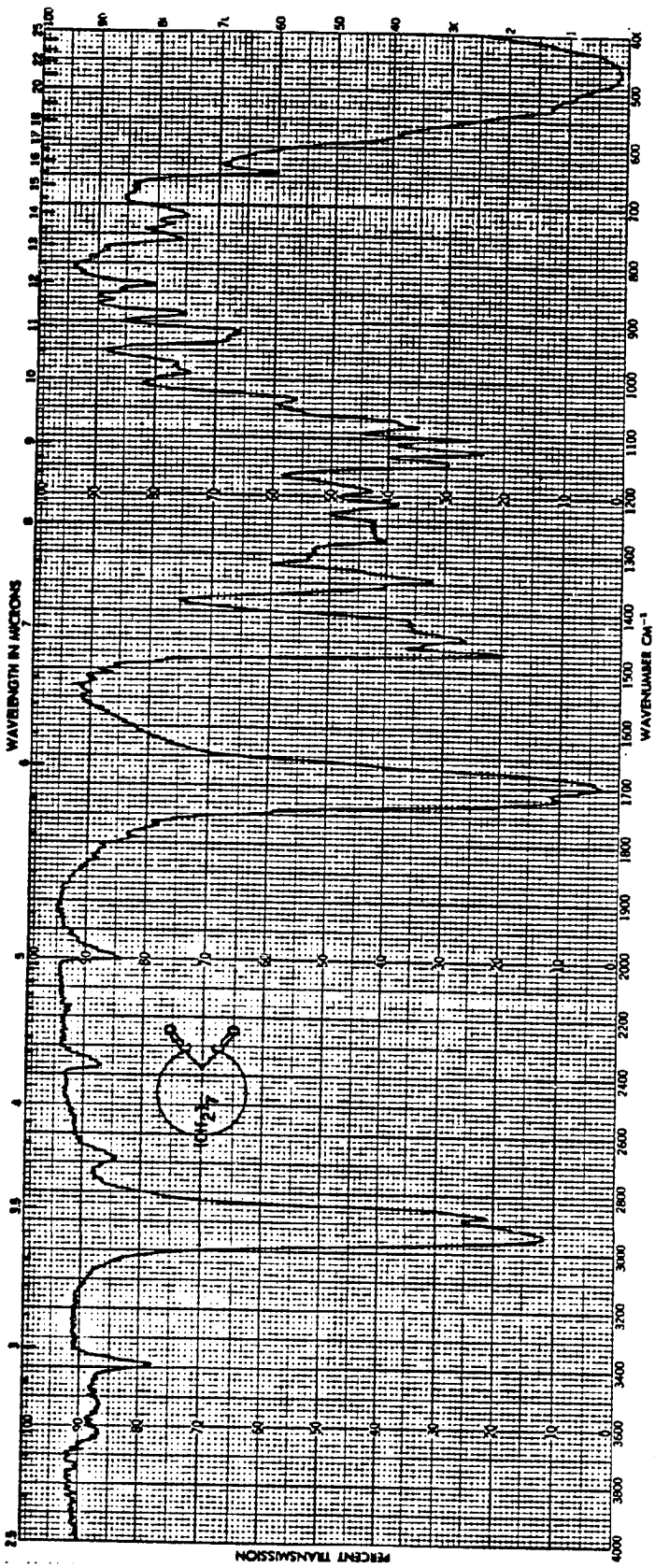
Infrared Spectra No. 11

Cycloheptane-1,3-dione



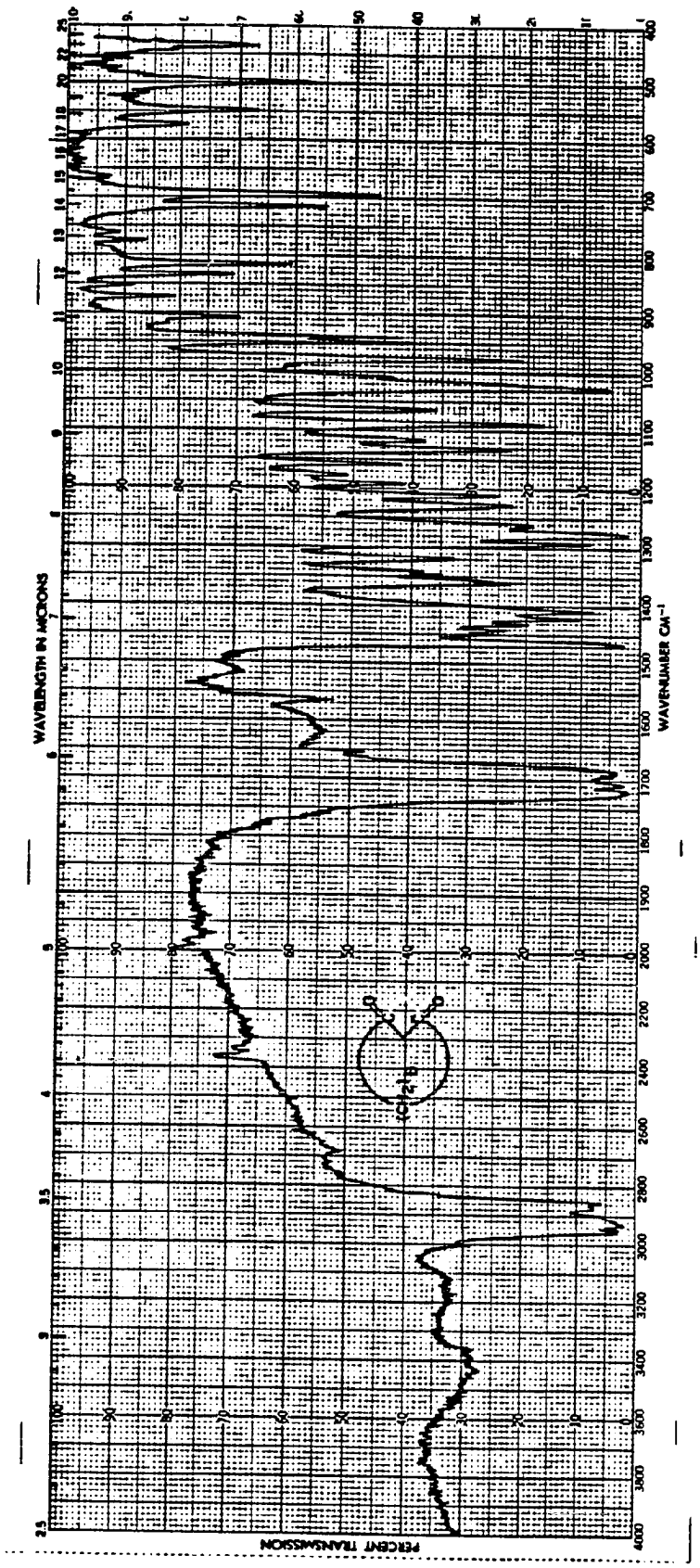
Infrared Spectra No. 12

Cyclononane-1,3-dione



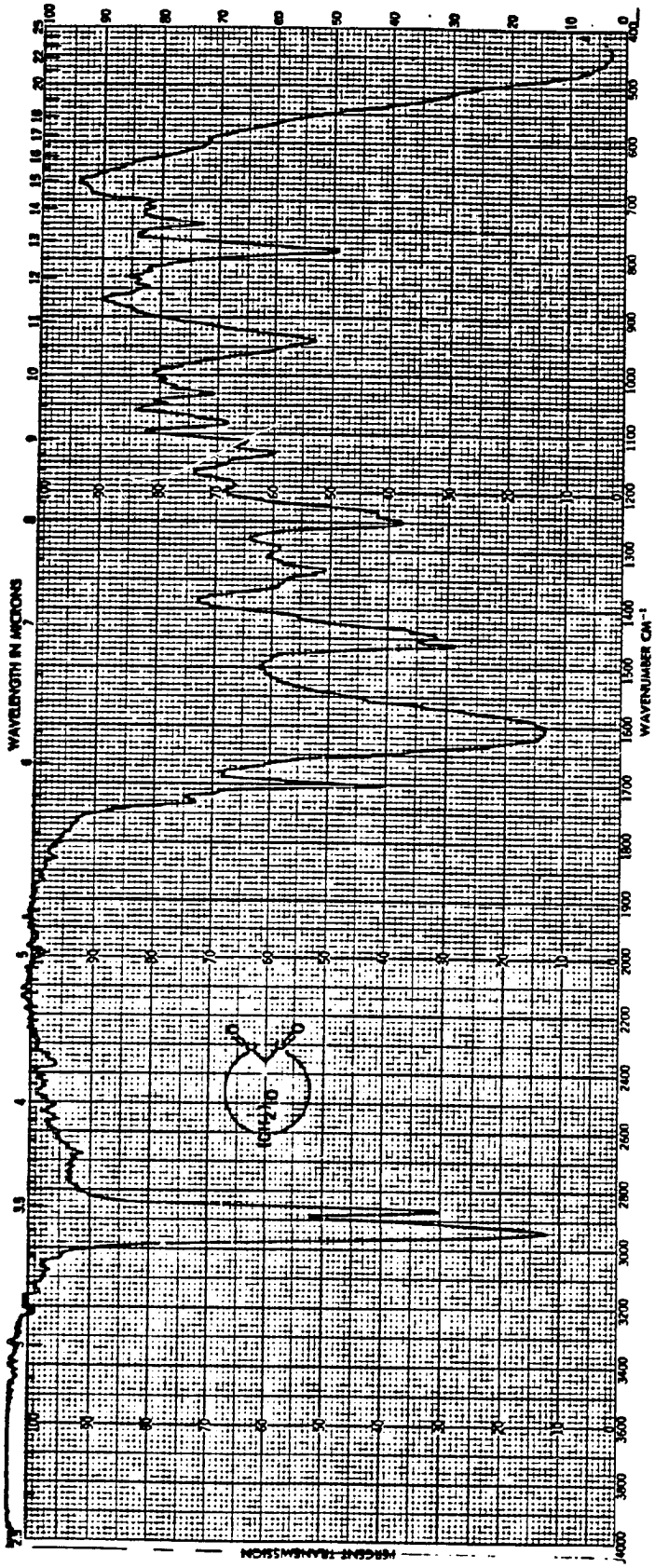
Infrared Spectra No. 13

Cyclodecane-1,3-dione



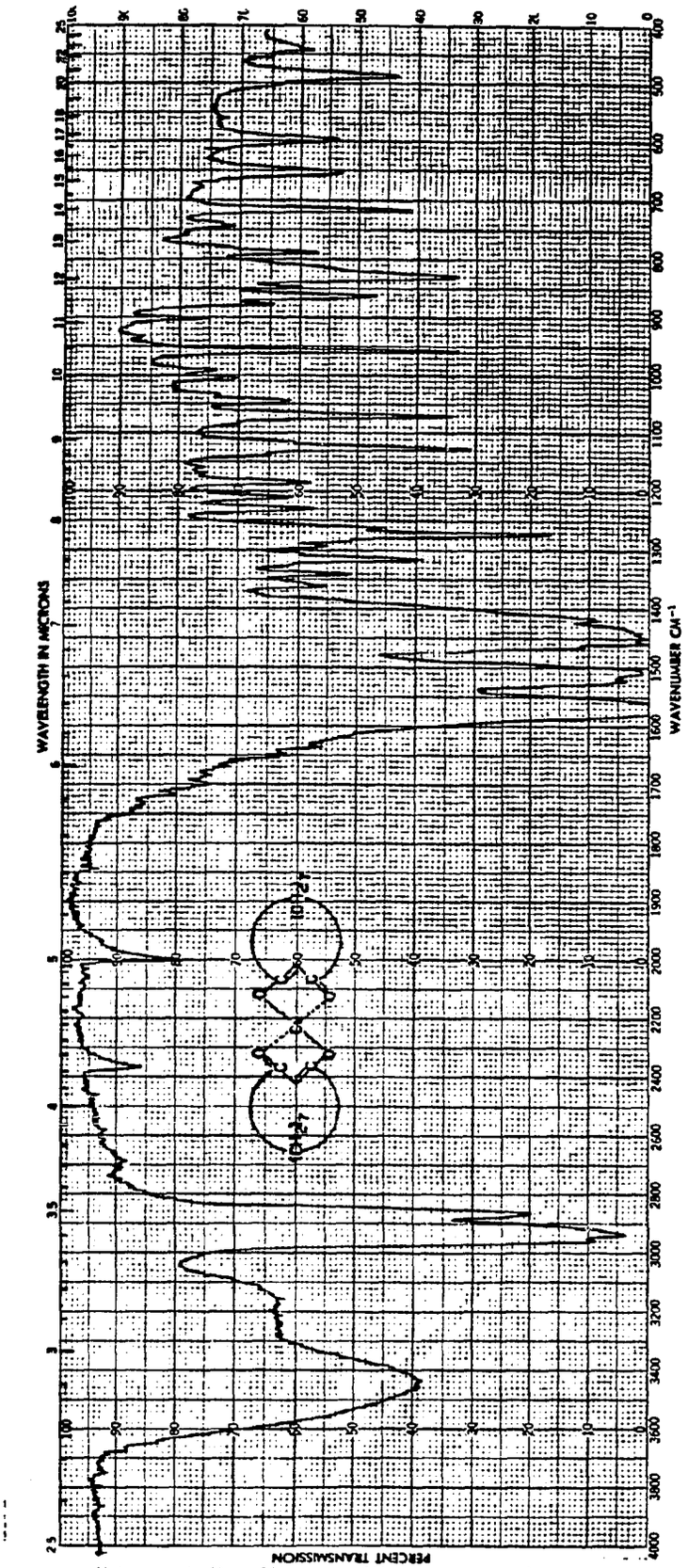
Infrared Spectra No. 14

Cycloundecane-1,3-dione



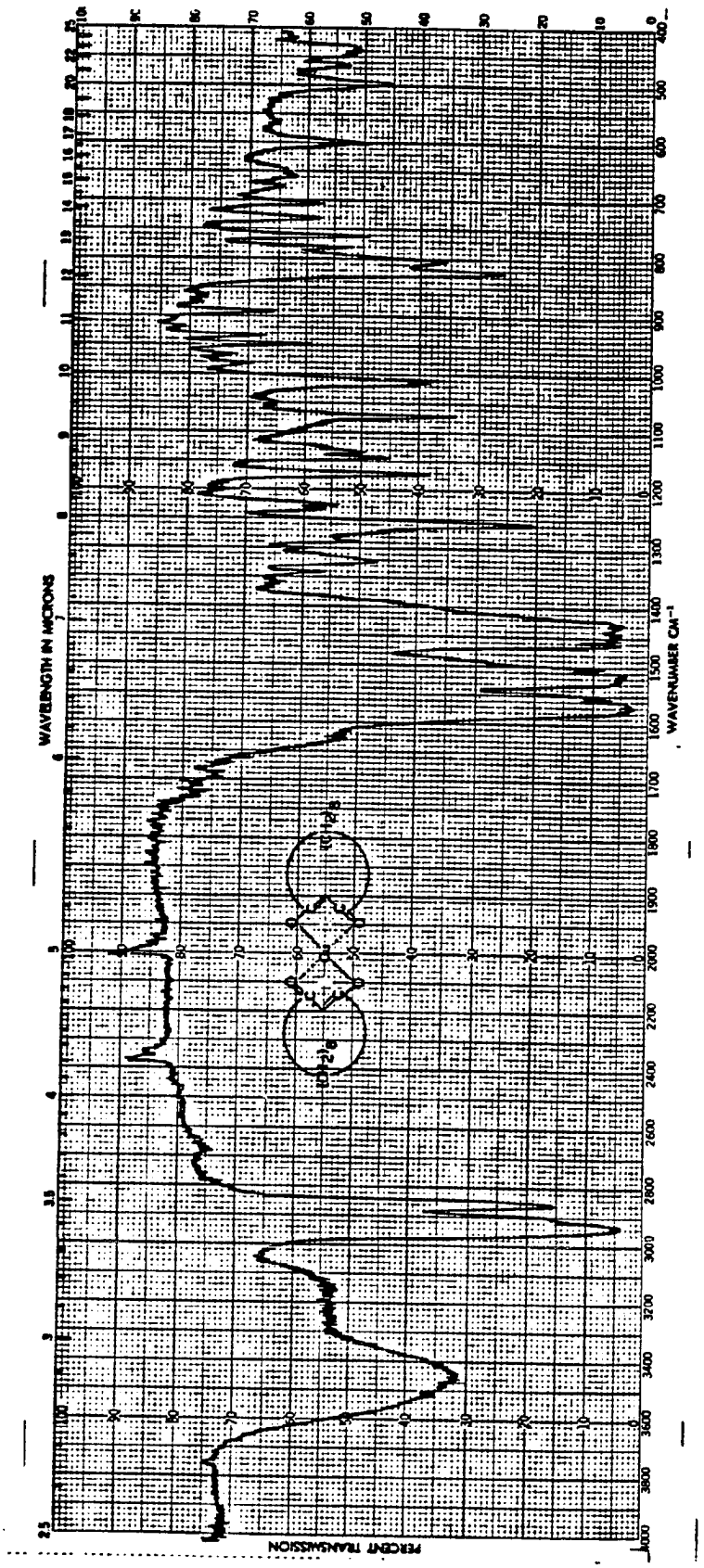
Infrared Spectra No. 15

Cyclotridecane-1,3-dione



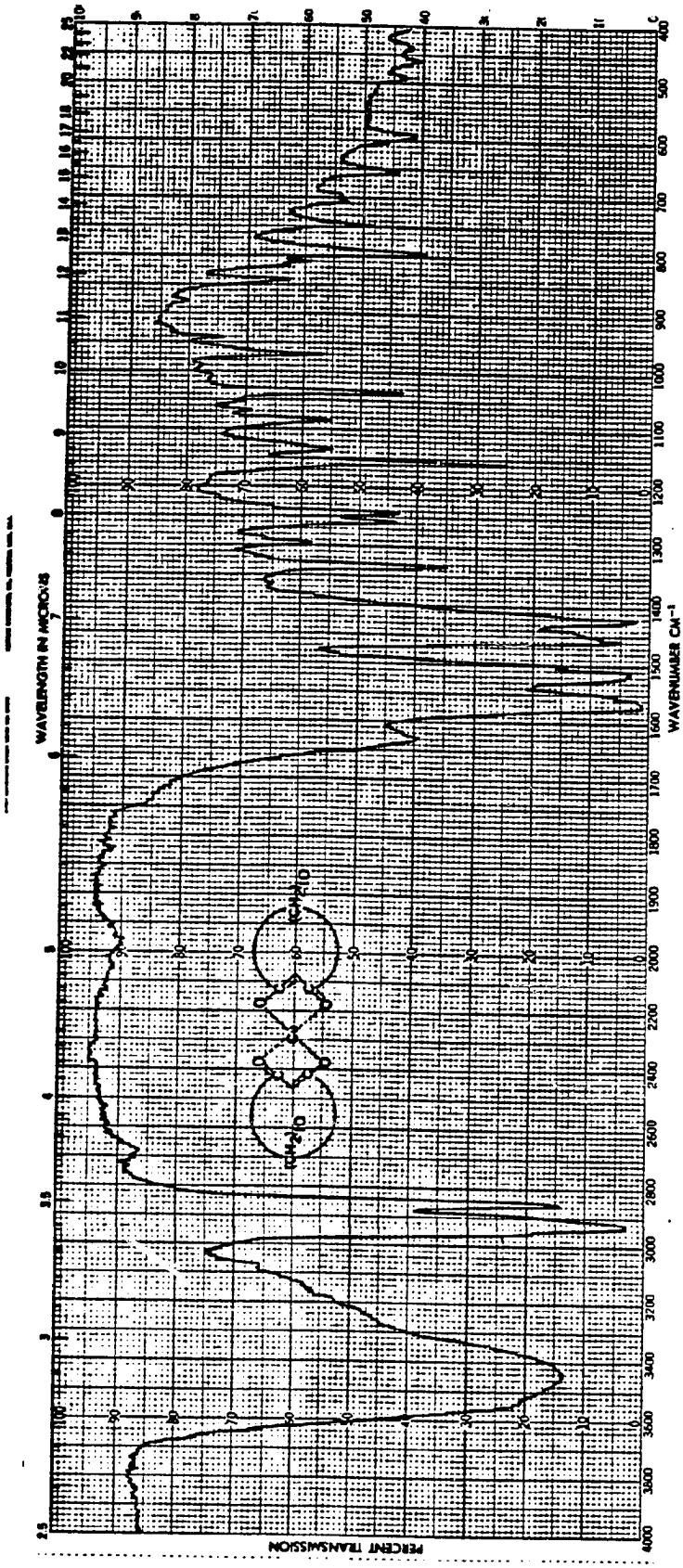
Infrared Spectra No. 16

Bis(cyclodecane-1,3-dionato)copper(II)



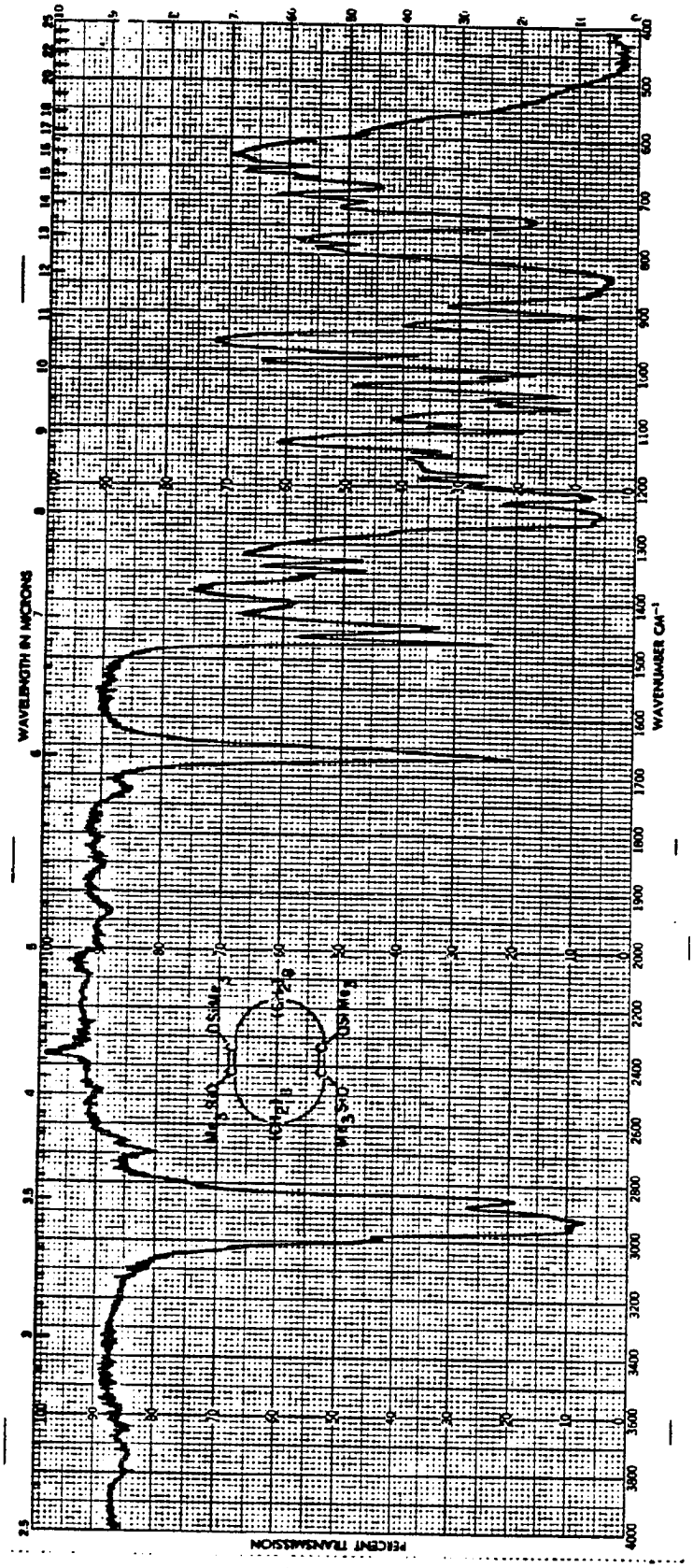
Infrared Spectra No. 17

Bis(cycloundeane-1,3-dionato)copper(II)



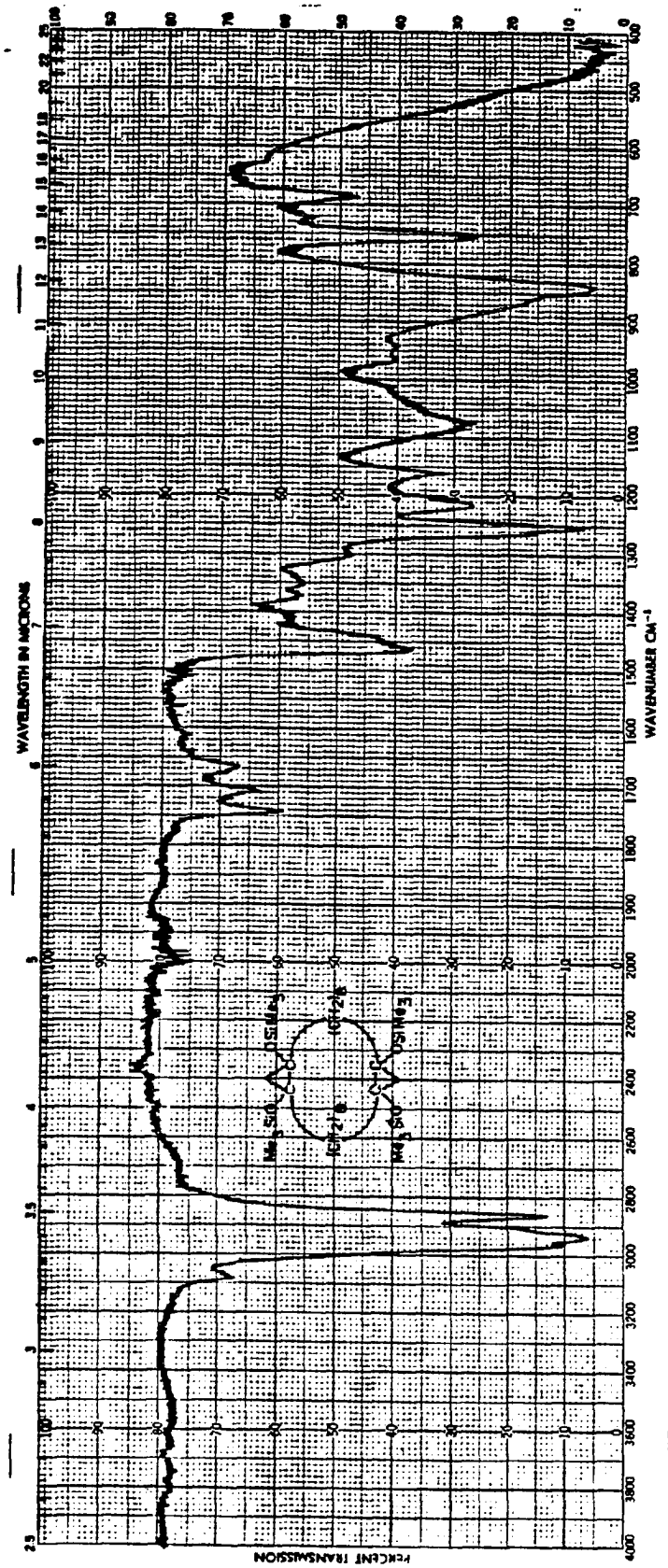
Infrared Spectra No. 18

Bis(cyclotridecane-1,3-dionato)copper(II)



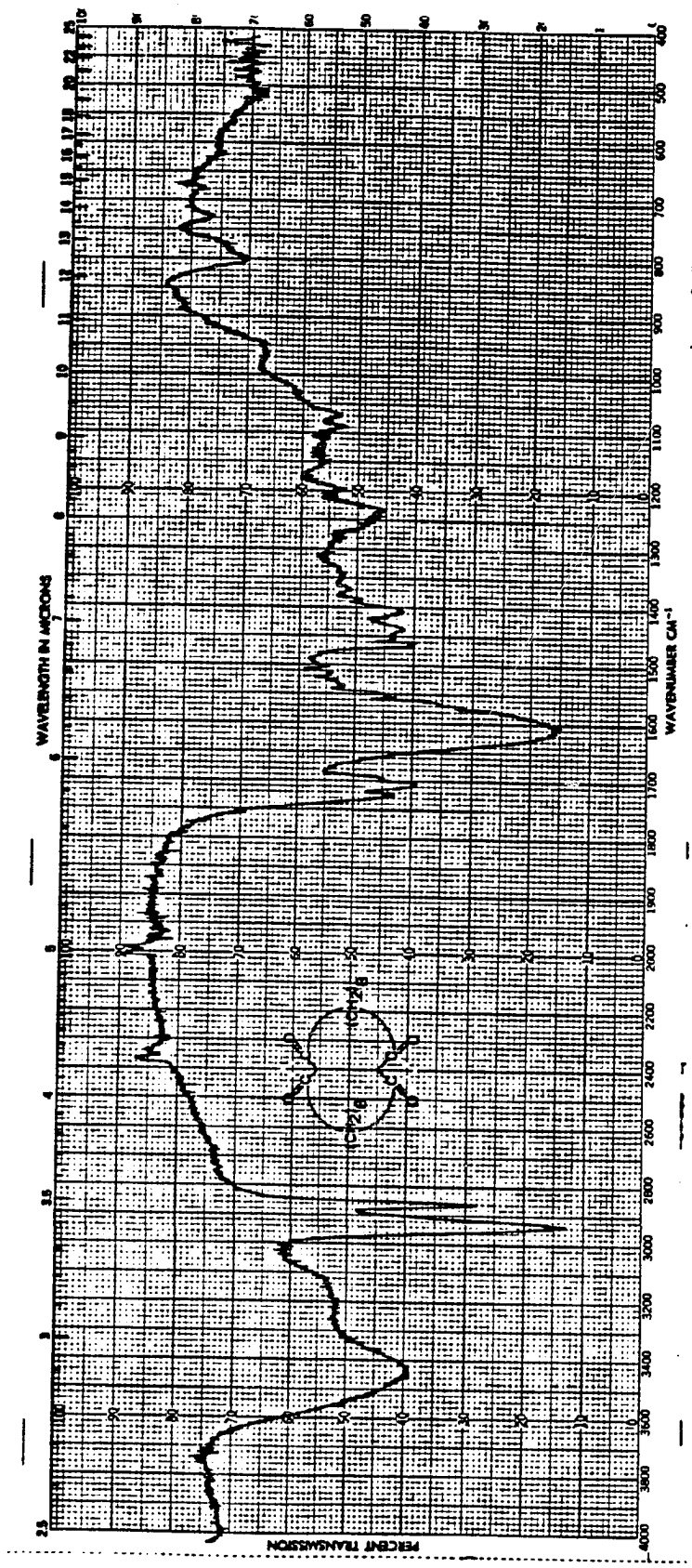
Infrared Spectra No. 19

Tetrakis(trimethylsilyloxy)cycloeicosadiene



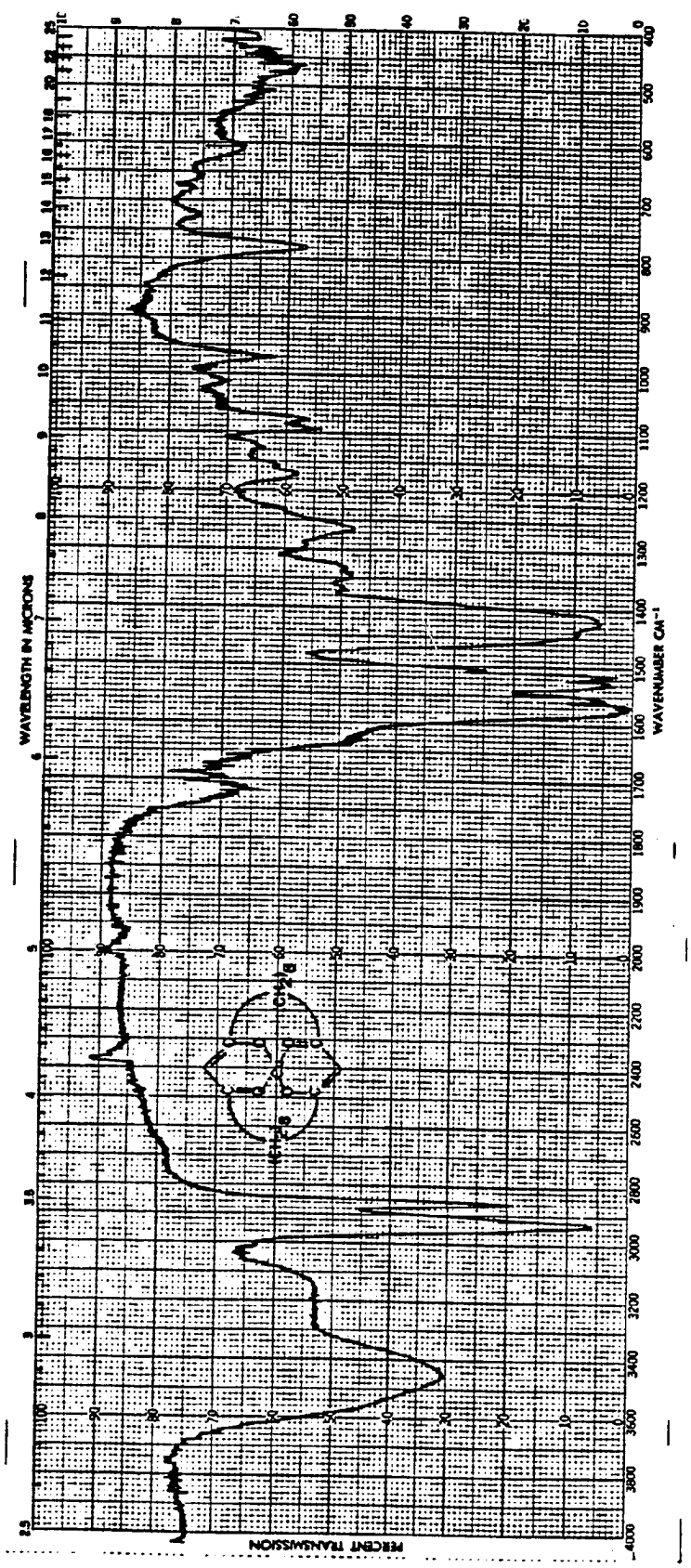
Infrared Spectra No. 20

Tetrakis(trimethylsilyloxy)tricyclo[8.8.1.1]docosane



Infrared Spectra No. 21

Cyclodocosane-1,3,12,14-tetraone



Infrared Spectra No. 22

(Cyclodocosane-1,3,12,14-tetraonato)copper(II)

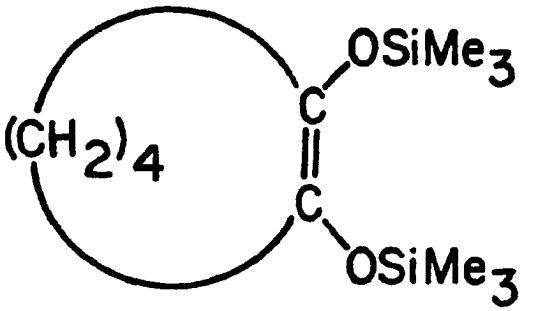
APPENDIX III

Mass Spectra

LIST OF MASS SPECTRA

Mass Spectra No. 1

1,2-Bis(trimethylsilyloxy)cyclohexene



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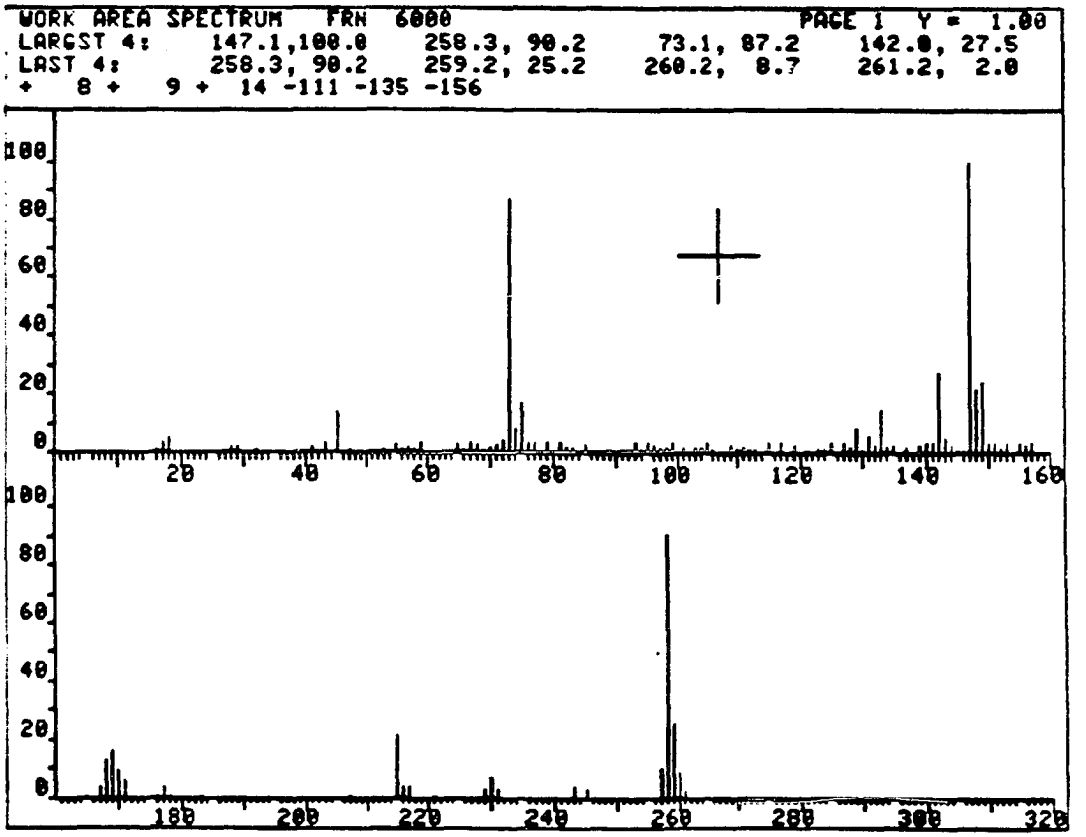


WORK AREA FRM 6000 + 8 + 9 + 14 -111 -135 -156
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
16	.7	72	4.6	105	3.3	140	3.4
17	2.9	73	87.2	106	.6	141	3.8
18	5.3	74	8.2	109	2.2	142	27.5
		75	17.2	110	.6	143	5.1
28	1.4			111	1.7	144	2.4
29	1.5	76	2.8	112	.9	145	.7
32	.5	77	3.5	113	1.1		
		79	3.4	115	3.2	146	1.0
41	1.5	81	3.6	117	2.9	147	100.0
43	3.1	82	1.4			148	21.8
45	13.8	83	1.7	119	2.2	149	24.1
47	.6	85	2.4	121	.6	150	3.1
		89	.6	123	.6	151	3.5
53	.6			124	.7	152	1.3
55	2.0	91	.8	125	3.7	153	3.3
56	.2	92	1.0	127	3.6	155	2.8
57	1.3	93	2.9	128	1.5	156	2.0
58	.6	94	.7	129	7.9	157	3.3
59	3.5	95	3.2	130	1.1		
		96	2.2	131	5.5	165	.6
65	2.3	97	1.9			167	3.8
66	.8	98	1.3	132	2.5	168	12.5
67	3.1	99	3.2	133	14.8	169	15.9
68	2.3	101	1.9	134	1.9	170	9.7
69	.5	103	1.9	135	2.6	171	6.4
70	2.0			137	2.0		
71	2.0	104	1.9	139	2.7	176	.7

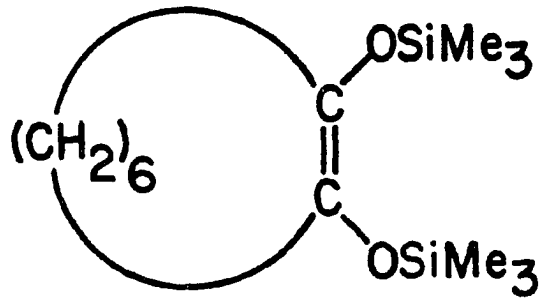
<CONT>

MASS	ABUND
177	3.9
178	.8
183	.7
207	.6
215	21.4
216	4.3
217	3.6
221	.5
229	3.0
230	7.2
231	2.5
243	3.7
245	2.6
257	10.3
258	90.2
259	25.2
260	8.7
261	2.0

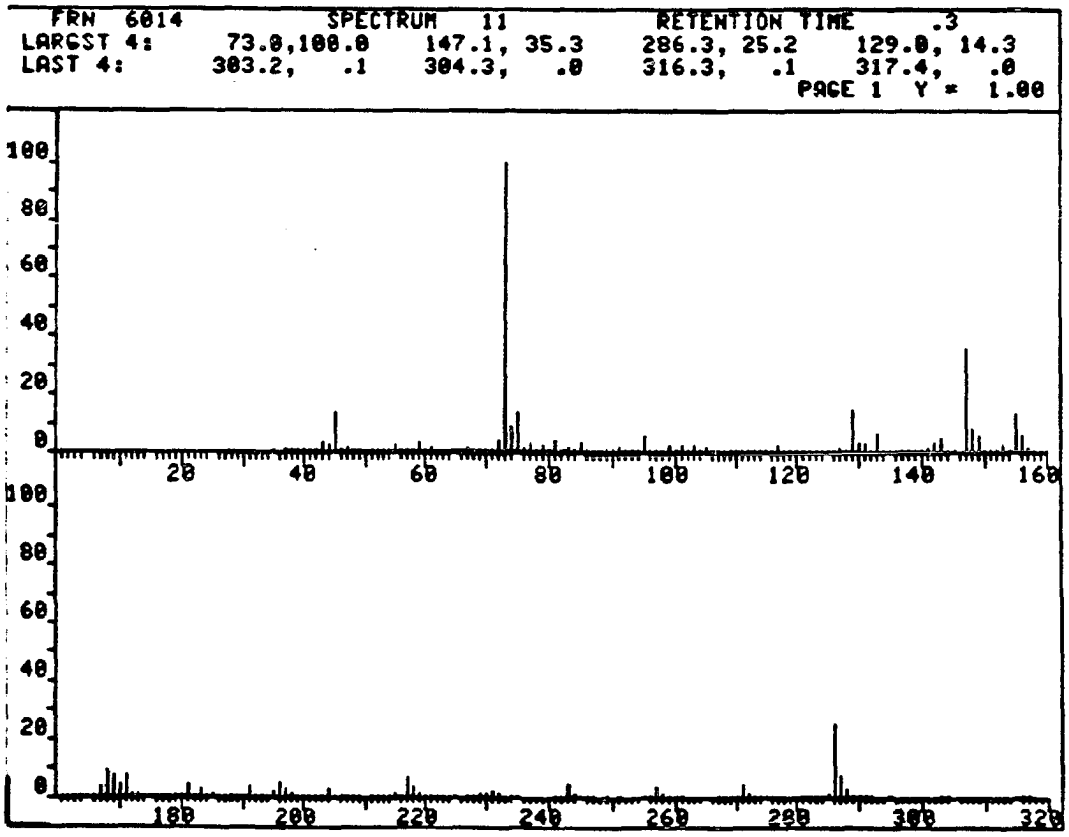
>PAUSE

Mass Spectra No. 2

1,2-Bis(trimethylsilyloxy)cyclooctene



M.W. = 286



FRN 6014 SPECTRUM 11 RET. TIME = .3
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
35	.1	62	.1	88	.3	113	1.2
37	.1	63	.1	89	.6	114	.5
38	.0	64	.1			115	1.3
39	.8	65	.8	90	.1	116	1.1
40	.2	66	.5	91	1.3	117	2.3
41	1.1	67	1.8	92	.4		
42	.7	68	.6	93	.8	118	.4
43	3.0	69	.8	94	.3	119	.7
44	2.6	70	.8	95	5.5	120	.2
45	13.6	71	1.1	96	.7	121	.3
46	1.1	72	4.6	97	.8	122	.1
47	1.5	73	100.0	98	.4	123	.3
		74	8.8	99	2.7	124	.1
48	.2	75	14.2	100	.6	125	.7
49	.1			101	2.2	126	.3
50	.1	76	1.5	102	.4	127	1.7
51	.2	77	3.5	103	2.3	128	.9
52	.2	78	.8			129	14.3
53	1.1	79	2.4	104	.5	130	2.8
54	.4	80	.8	105	1.7	131	3.7
55	2.1	81	4.1	106	1.1		
56	.4	82	.4	107	.8	132	1.0
57	1.1	83	1.5	108	.3	133	6.7
58	1.3	84	.5	109	1.2	134	1.0
59	3.4	85	3.8	110	.2	135	.6
60	.7	86	.5	111	1.3	136	.2
61	1.5	87	.8	112	.4	137	.3
						<CONT>	

FRN 6014 SPECTRUM 11 RET. TIME = .3
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
138	.2	164	.1	189	.3	216	.3
139	.7	165	.5	190	.1	217	6.7
140	.6	166	.2	191	3.7	218	4.1
141	1.4	167	4.1	192	.7	219	1.4
142	3.4	168	9.4	193	.5	220	.4
143	4.9	169	7.9	194	.1	221	.4
144	1.3	170	4.4	195	2.1	222	.1
145	.6	171	7.4	196	5.6	223	.1
		172	1.2	197	2.8	224	.0
147	35.3	173	1.3	198	1.6	225	.0
148	7.7			199	.6	227	.2
149	5.8	174	.2	200	.2	228	.1
150	.6	175	.2	201	.2	229	1.6
151	1.0	176	.1				
152	.3	177	.5	202	.1	230	1.1
153	2.0	178	.1	203	.4	231	1.7
154	1.3	179	.2	204	3.0	232	1.3
155	13.0	180	.1	205	.6	233	.4
156	5.5	181	4.3	206	.3	234	.1
157	1.9	182	.7	207	.6	235	.0
158	.3	183	3.4	208	.1	241	.1
159	.2	184	.6	209	.1	242	.1
		185	1.0	211	.1	243	4.3
160	.1	186	.2	212	.1		
161	.1	187	.2	213	.4	244	1.4
162	.0			214	.1	245	.5
163	.3	188	.1	215	1.2	246	.1
						<CONT>	

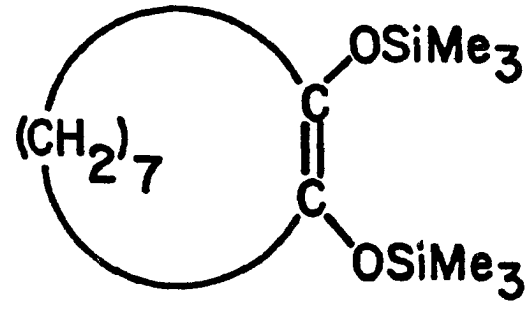
FRN 6014 SPECTRUM 11 RET. TIME = .3

MASS	ABUND
247	.1
249	.0
251	.1
255	.1
256	.1
257	4.0
258	1.1
259	.8
260	.1
261	.1
267	.1
268	.1
269	.1
270	.1
271	4.8
272	1.2
273	.6
274	.1
275	.3
276	.1
277	.1
278	.0
281	.1
282	.8
283	.0
284	.1
285	1.1
286	25.2
287	8.1
288	2.8
289	.5
290	.1
291	.1
292	.0
295	.0
303	.1
304	.0
316	.1
317	.0

>PAUSE

Mass Spectra No. 3

1,2-Bis(trimethylsilyloxy)cyclononene



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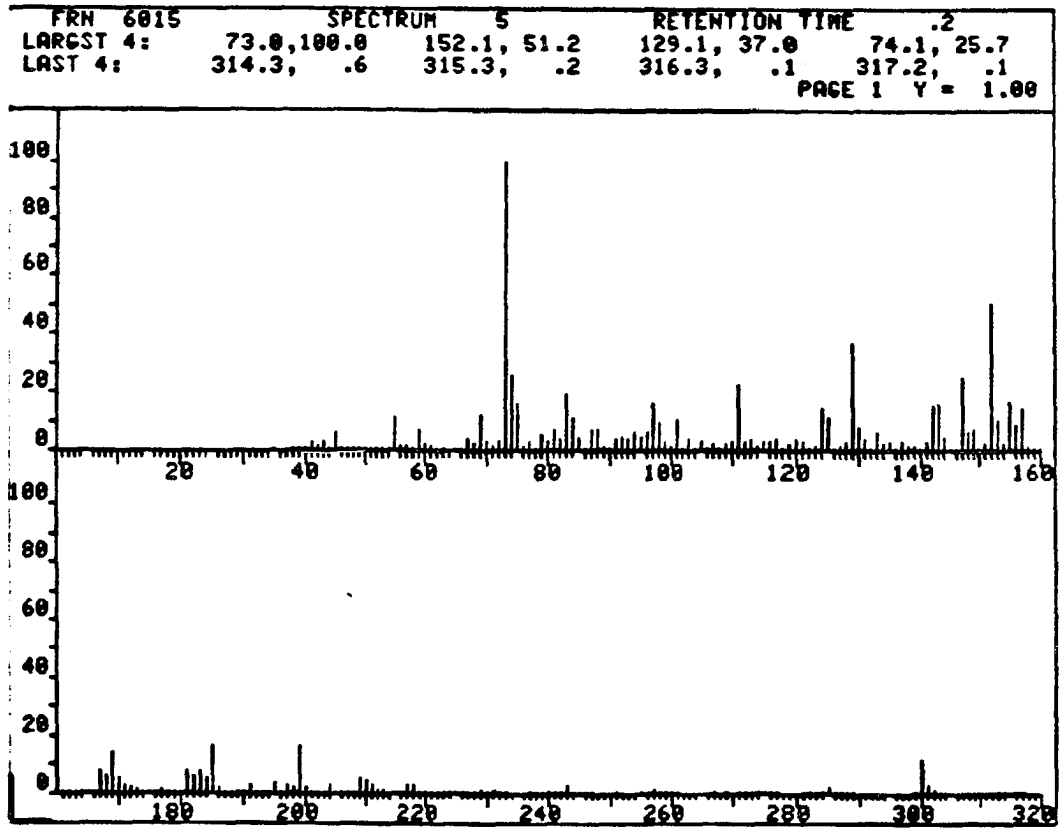


FRN 6015 SPECTRUM 5 RET. TIME = .2
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
35	.1	62	.1	89	1.4	114	1.5
38	.1	63	.5			115	3.4
39	1.1	65	.9	90	.2	116	2.8
40	.4	66	.5	91	4.2	117	4.3
41	3.7	67	4.6	92	4.9		
42	1.9	68	2.7	93	4.3	118	.7
43	3.5	69	12.4	94	6.7	119	2.2
44	.9	70	3.8	95	5.0	120	4.4
45	6.8	71	1.7	96	6.6	121	3.0
46	.4	72	3.5	97	16.3	122	1.1
47	1.0	73	100.0	98	9.6	123	1.6
		74	25.7	99	3.6	124	14.3
48	.2	75	16.1	100	1.4	125	11.0
49	.1			101	10.6	126	1.3
50	.1	76	1.7	102	1.2	127	1.9
51	.1	77	2.8	103	3.9	128	3.8
52	.2	78	1.0			129	37.0
53	1.2	79	5.9	104	.9	130	7.7
54	1.0	80	2.9	105	3.7	131	4.1
55	11.3	81	7.3	106	1.0		
56	1.9	82	4.5	107	2.7	132	1.2
57	2.0	83	19.8	108	1.3	133	6.3
58	.9	84	11.5	109	2.3	134	2.2
59	6.9	85	4.9	110	3.8	135	3.5
60	2.4	86	.7	111	22.4	136	1.1
61	1.7	87	7.4	112	3.0	137	3.4
		88	7.1	113	4.0	138	1.3
						<CONT>	

FRN 6015 SPECTRUM 5 RET. TIME = .2
>PAUSE

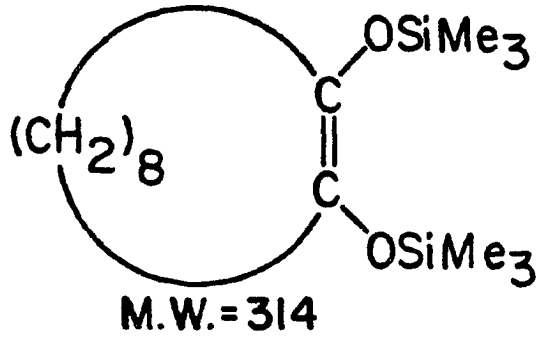
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
139	1.6	164	.1	189	.4	215	.7
140	1.1	165	.5	190	.1		
141	3.0	166	.6	191	2.9	216	.2
142	15.2	167	7.5	192	.6	217	2.6
143	16.5	168	6.1	193	.4	218	2.5
144	4.8	169	14.0	194	.1	219	.9
145	1.2	170	5.1	195	4.0	220	.3
		171	3.3	196	.9	221	.3
146	.5	172	1.7	197	2.8	222	.1
147	25.1	173	.9	198	2.2	223	.2
148	6.5			199	16.3	224	.1
149	7.0	174	.2	200	1.9	225	.2
150	1.0	175	.2	201	.9	226	.1
151	2.5	176	.4			227	.6
152	51.2	177	1.1	202	.3	228	.1
153	10.7	178	.2	203	.7	229	1.1
154	2.5	179	.3	204	3.4		
155	17.5	180	.3	205	.8	230	.5
156	9.0	181	7.3	206	.3	231	1.1
157	14.3	182	5.8	207	.4	232	.3
158	1.5	183	7.6	208	.2	233	.1
159	.6	184	5.2	209	5.3	237	.1
		185	16.6	210	5.0	238	.1
160	.5	186	1.8	211	2.7	239	.1
161	.1	187	.6	212	1.3	240	.0
162	.1			213	1.2	241	.1
163	.3	188	.4	214	.3	242	.1
						<CONT>	

FRH 6015 SPECTRUM 5 RET. TIME = .2

MASS	ABUND	MASS	ABUND
243	2.6	283	.1
		284	.1
244	.8	285	1.9
245	.4		
246	.1	286	.6
247	.0	287	.5
251	.1	288	.2
255	.1	289	.1
256	.1	299	.5
257	1.4		
		300	11.9
258	.3	301	3.1
259	.6	302	1.1
260	.2	303	.3
261	.0	304	.0
267	.1	313	.2
269	.0		
271	.4	314	.6
		315	.2
272	.3	316	.1
273	.5	317	.1
274	.1	>PAUSE	
275	.1		
276	.0		
277	.0		
281	.1		
282	.0		

Mass Spectra No. 4

1,2-Bis(trimethylsilyloxy)cyclodecene



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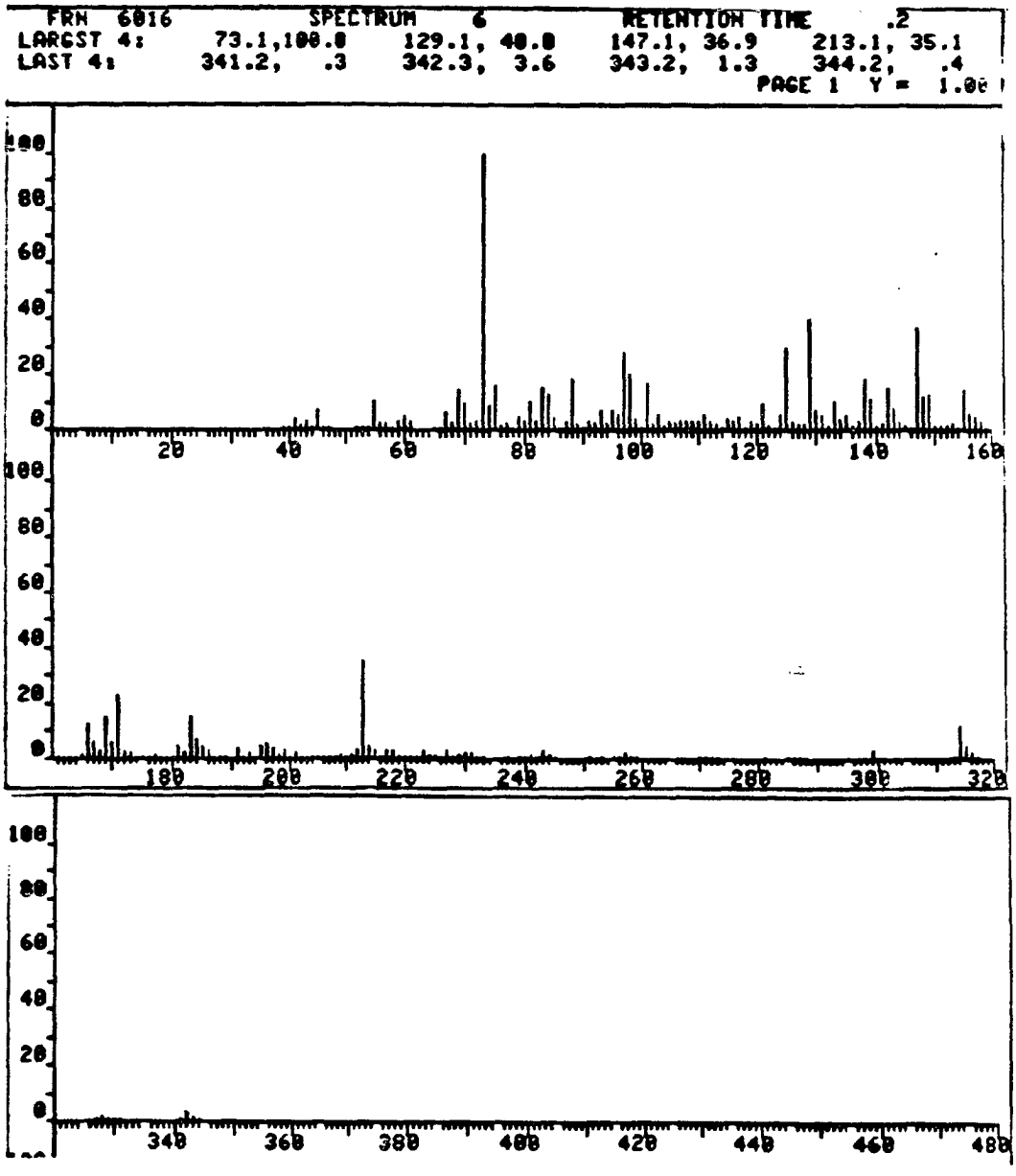


FRN 6016 SPECTRUM 6 RET. TIME = .2
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
39	1.0	70	10.1	95	7.3	120	2.2
		71	2.7	96	5.6	121	9.6
40	.4	72	3.7	97	20.3	122	1.3
41	4.4	73	100.0	98	20.3	123	1.3
42	1.8	74	9.1	99	4.0	124	5.9
43	3.5	75	15.8	100	1.0	125	30.1
44	1.3			101	16.5	126	2.9
45	7.3	76	1.6	102	2.4	127	2.1
46	.5	77	2.2	103	5.5	128	2.6
47	.9	78	.7			129	40.0
		79	5.0	104	1.3	130	6.9
52	.2	80	2.8	105	3.3	131	5.5
53	1.1	81	10.7	106	2.1		
54	1.2	82	2.9	107	3.6	132	2.0
55	10.9	83	15.1	108	3.3	133	10.8
56	2.5	84	13.5	109	3.2	134	4.5
57	2.6	85	5.0	110	3.7	135	5.9
58	.9	86	.8	111	5.6	136	1.7
59	3.1	87	2.9	112	3.7	137	3.3
60	5.0	88	18.7	113	2.5	138	18.9
61	3.7	89	2.6	114	1.1	139	11.1
				115	4.5	140	1.8
65	.7	90	.3	116	3.0	141	2.3
66	.5	91	3.5	117	4.8	142	15.7
67	6.3	92	2.7			143	8.3
68	2.6	93	7.5	118	.8	144	2.8
69	14.3	94	2.5	119	3.8	145	1.5
						<CONT>	

FRN 6016 SPECTRUM 6 RET. TIME = .2
>PAUSE

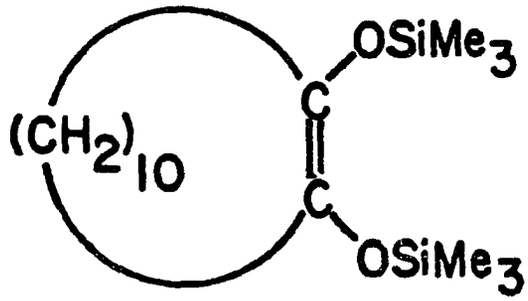
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
146	.7	172	3.2	198	1.1	223	3.0
147	36.9	173	1.8	199	2.6	224	1.4
148	11.7			200	.6	225	1.1
149	12.7	174	.4	201	1.7	226	.7
150	1.8	175	.3			227	3.5
151	1.5	176	.4	202	.7	228	.9
152	2.0	177	1.1	203	.8	229	1.3
153	2.6	178	.4	204	.7		
154	1.2	179	.5	205	.4	230	1.7
155	14.6	180	.4	206	.2	231	1.7
156	6.0	181	4.6	207	.8	232	.6
157	5.2	182	2.1	208	.2	233	.2
158	3.5	183	15.1	209	1.5	237	.2
159	.9	184	6.9	210	.5	239	.3
		185	4.7	211	1.4	240	.2
160	.5	186	2.8	212	3.2	241	1.0
161	.3	187	.7	213	35.1	242	.4
162	.2			214	4.8	243	2.8
163	.6	188	.2	215	2.7		
164	.2	189	.3			244	1.0
165	1.2	191	4.2	216	.7	245	.4
166	13.0	192	.9	217	2.7	251	.2
167	5.9	193	1.8	218	3.0	253	.2
168	3.3	194	.9	219	1.0	255	.3
169	14.7	195	4.4	220	.3	256	.2
170	6.4	196	5.4	221	.8	257	1.9
171	23.2	197	4.2	222	.4		
						<CONT>	

FRM 6016 SPECTRUM 6 RET. TIME = .2

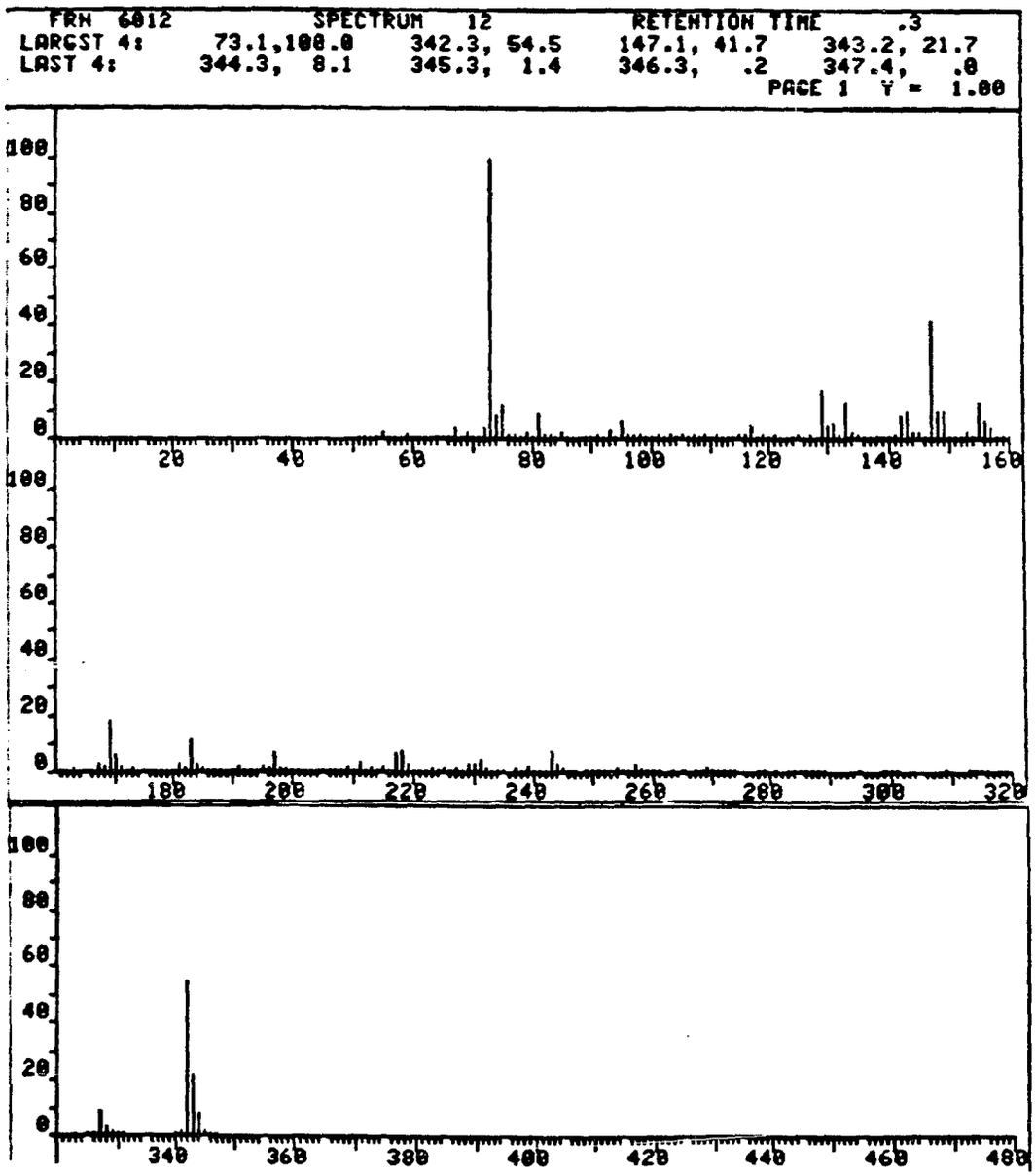
MASS	ABUND	MASS	ABUND
258	.5	328	2.0
259	.5	329	.6
270	.2	330	.2
271	.6	331	.2
		341	.3
272	.2		
273	.6	342	3.6
281	.3	343	1.3
285	.3	344	.4
		>PAUSE	
286	.2		
287	.9		
288	.3		
295	.3		
299	2.6		
300	.8		
301	.4		
303	.2		
313	.8		
314	11.6		
315	4.3		
316	1.7		
317	.3		
327	.5		

Mass Spectra No. 5

1,2-Bis(trimethylsilyoxy)cyclododecene



M.W.= 342



FRM 6012 SPECTRUM 12 RET. TIME = .3
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
51	.0	76	1.4	102	.4	127	1.4
52	.1	77	1.9	103	1.8	128	.9
53	.5	78	.4			129	16.7
54	.4	79	2.2	104	.4	130	5.0
55	2.5	80	1.3	105	2.0	131	6.1
56	.7	81	9.0	106	.5		
57	1.0	82	1.5	107	1.4	132	2.0
58	.6	83	2.0	108	.7	133	12.9
59	1.4	84	1.2	109	1.9	134	2.1
60	.5	85	2.5	110	.5	135	1.7
61	.7	86	.3	111	1.9	136	.7
		87	.5	112	1.0	137	.7
62	.0	88	.3	113	1.1	138	.3
63	.1	89	.6	114	.5	139	.8
64	.1			115	1.5	140	.6
65	.6	90	.1	116	1.3	141	1.9
66	.4	91	1.8	117	5.2	142	7.8
67	4.1	92	.7			143	10.0
68	1.0	93	2.9	118	.7	144	2.6
69	2.8	94	1.2	119	1.7	145	2.3
70	1.0	95	6.4	120	.7		
71	1.3	96	1.3	121	2.0	146	.8
72	4.4	97	1.8	122	.5	147	41.7
73	100.0	98	1.8	123	.4	148	9.7
74	8.2	99	1.2	124	.4	149	9.6
75	11.7	100	.4	125	1.3	150	1.1
		101	1.8	126	.5	151	1.1
						<CONT>	

FRM 6012 SPECTRUM 12 RET. TIME = .3
>PAUSE

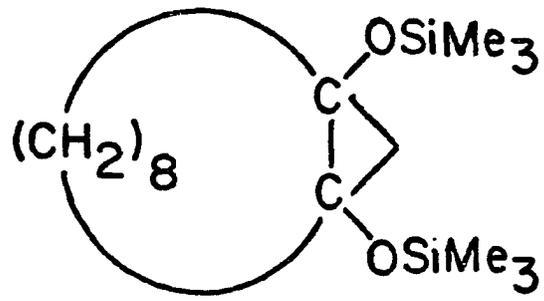
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
152	.5	177	.7	202	.3	228	.3
153	2.7	178	.2	203	.9	229	2.8
154	.9	179	.3	204	.7		
155	12.5	180	.1	205	.9	230	2.4
156	6.3	181	2.8	206	.2	231	4.4
157	4.2	182	1.2	207	.5	232	1.5
158	.7	183	11.4	208	.2	233	.4
159	.7	184	2.6	209	1.9	234	.1
		185	1.3	210	.5	235	.1
160	.3	186	.3	211	4.2	237	1.1
161	.7	187	.4	212	.8	238	.2
162	.5			213	1.1	239	2.0
163	1.3	188	.1	214	.3	240	.6
164	.3	189	.4	215	2.4	241	.7
165	.6	190	.1			242	.4
166	.3	191	1.8	216	.5	243	7.9
167	2.6	192	.4	217	6.8		
168	2.1	193	.4	218	8.0	244	2.6
169	18.2	194	.2	219	2.5	245	1.0
170	6.4	195	2.2	220	.7	246	.2
171	2.2	196	1.3	221	.6	247	.1
172	.6	197	6.7	222	.2	249	.1
173	1.3	198	1.4	223	1.4	250	.1
		199	1.2	224	.6	251	.5
174	.2	200	.2	225	1.3	252	.3
175	.1	201	.9	226	.3	253	.9
176	.2			227	1.3	254	1.2
						<CONT>	

FRN 6012 SPECTRUM 12 RET. TIME = .3

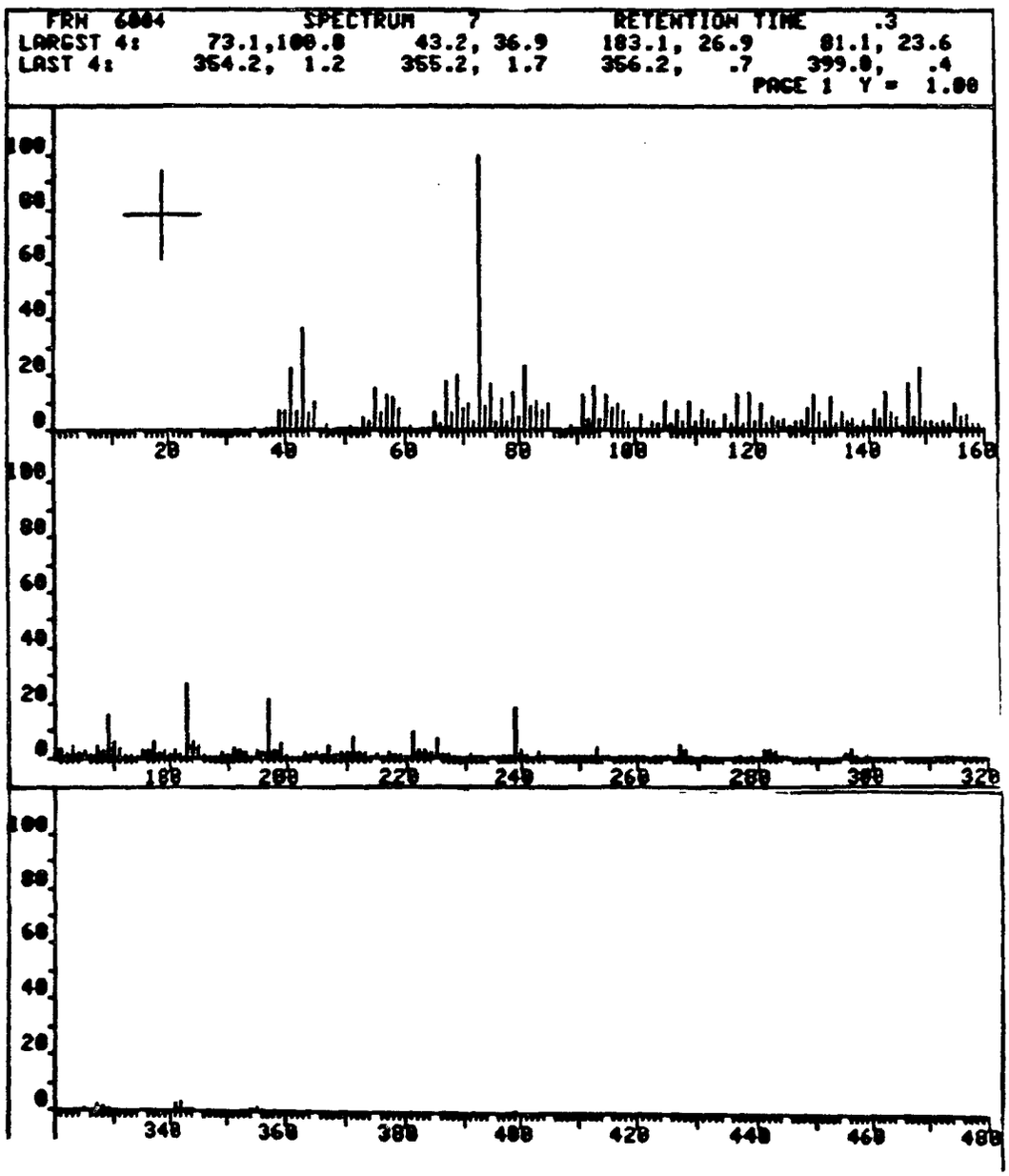
MASS	ABUND	MASS	ABUND	MASS	ABUND
255	.9	287	.5	343	21.7
256	.3	288	.1	344	8.1
257	3.1	289	.0	345	1.4
		295	.0	346	.2
258	.9	299	.5	347	.0
259	.6			>PAUSE	
260	.1	300	.1		
261	.1	301	.1		
263	.1	309	.0		
265	.1	313	.3		
267	.2				
268	.2	314	.2		
269	1.0	315	.3		
270	.4	316	.1		
271	.8	323	.0		
		325	.1		
272	.2	326	.1		
273	.2	327	9.1		
274	.1				
278	.0	328	3.8		
279	.0	329	1.3		
281	.0	330	.3		
283	.1	331	.1		
284	.0	340	.1		
285	.4	341	1.5		
286	.1	342	54.5		

Mass Spectra No. 6

1,10-Bis(trimethylsilyloxy)bicyclo[8.1.0]undecane



M.W. = 329



FRM 6004 SPECTRUM 7 RET. TIME = .3
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
35	1.2	63	1.0	90	.6	116	2.1
37	1.0	64	.8	91	13.4	117	12.5
38	.8	65	6.6	92	4.2		
39	7.1	66	2.4	93	16.1	118	2.5
40	7.1	67	18.0	94	4.1	119	13.9
41	22.8	68	6.4	95	13.2	120	3.0
42	7.4	69	20.3	96	7.8	121	10.1
43	36.9	70	7.7	97	9.7	122	2.7
44	6.3	71	9.7	98	7.2	123	4.7
45	10.3	72	3.6	99	2.8	124	3.2
46	.6	73	100.0	100	1.1	125	4.6
47	2.7	74	9.0	101	5.7	126	1.8
		75	16.9	102	1.0	127	3.3
49	.7			103	2.9	128	3.7
50	.7	76	3.8			129	8.0
51	1.9	77	11.5	104	2.1	130	13.2
52	.9	78	2.8	105	10.9	131	6.8
53	5.0	79	13.7	106	2.5		
54	2.8	80	4.9	107	7.0	132	2.8
55	15.6	81	23.6	108	3.9	133	12.4
56	6.2	82	9.3	109	10.9	134	2.5
57	12.9	83	10.9	110	3.5	135	6.8
58	12.0	84	7.2	111	7.0	136	3.3
59	7.7	85	9.8	112	3.9	137	4.5
60	.7	86	1.0	113	2.9	138	1.5
61	1.8	87	.7	114	.6	139	3.1
		89	1.9	115	5.6	140	1.9
						<CONT>	

FRM 6004 SPECTRUM 7 RET. TIME = .3
>PAUSE

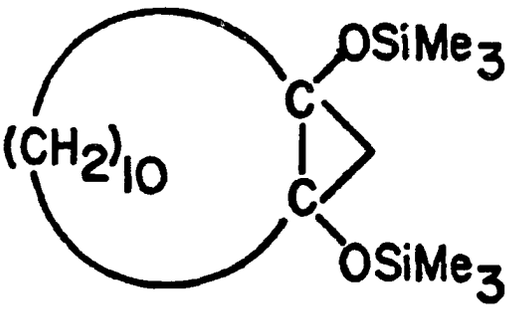
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
141	7.0	166	1.4	191	4.0	216	.6
142	4.0	167	4.6	192	2.7	217	2.0
143	14.2	168	2.7	193	2.3	218	1.2
144	6.2	169	15.9	194	.9	219	1.4
145	4.7	170	6.0	195	3.5	220	.8
		171	4.1	196	1.9	221	9.1
146	1.7	172	1.5	197	21.3	222	2.9
147	17.1	173	1.4	198	3.5	223	2.5
148	4.9			199	5.2	224	1.7
149	23.0	174	.6	200	1.0	225	6.9
150	3.6	175	2.0	201	.5	226	1.4
151	3.0	176	3.0			227	1.1
152	2.1	177	6.3	202	.6	228	.4
153	3.0	178	1.9	203	2.2	229	.7
154	2.2	179	2.6	204	1.4		
155	9.5	180	1.2	205	1.9	231	1.2
156	5.0	181	2.7	206	1.2	232	.8
157	6.0	182	1.6	207	4.7	233	.6
158	2.3	183	26.9	208	1.2	235	.6
159	2.3	184	6.1	209	1.9	236	.7
		185	4.6	210	1.7	237	.8
160	1.1	186	1.0	211	0.3	238	.8
161	3.7	187	.9	212	2.0	239	18.6
162	1.7			213	1.7	240	3.3
163	4.0	188	.4	214	.4	241	1.5
164	1.7	189	1.0	215	1.5	243	1.9
165	3.1	190	1.3				
						<CONT>	

FRN 6004 SPECTRUM 7 RET. TIME = .3

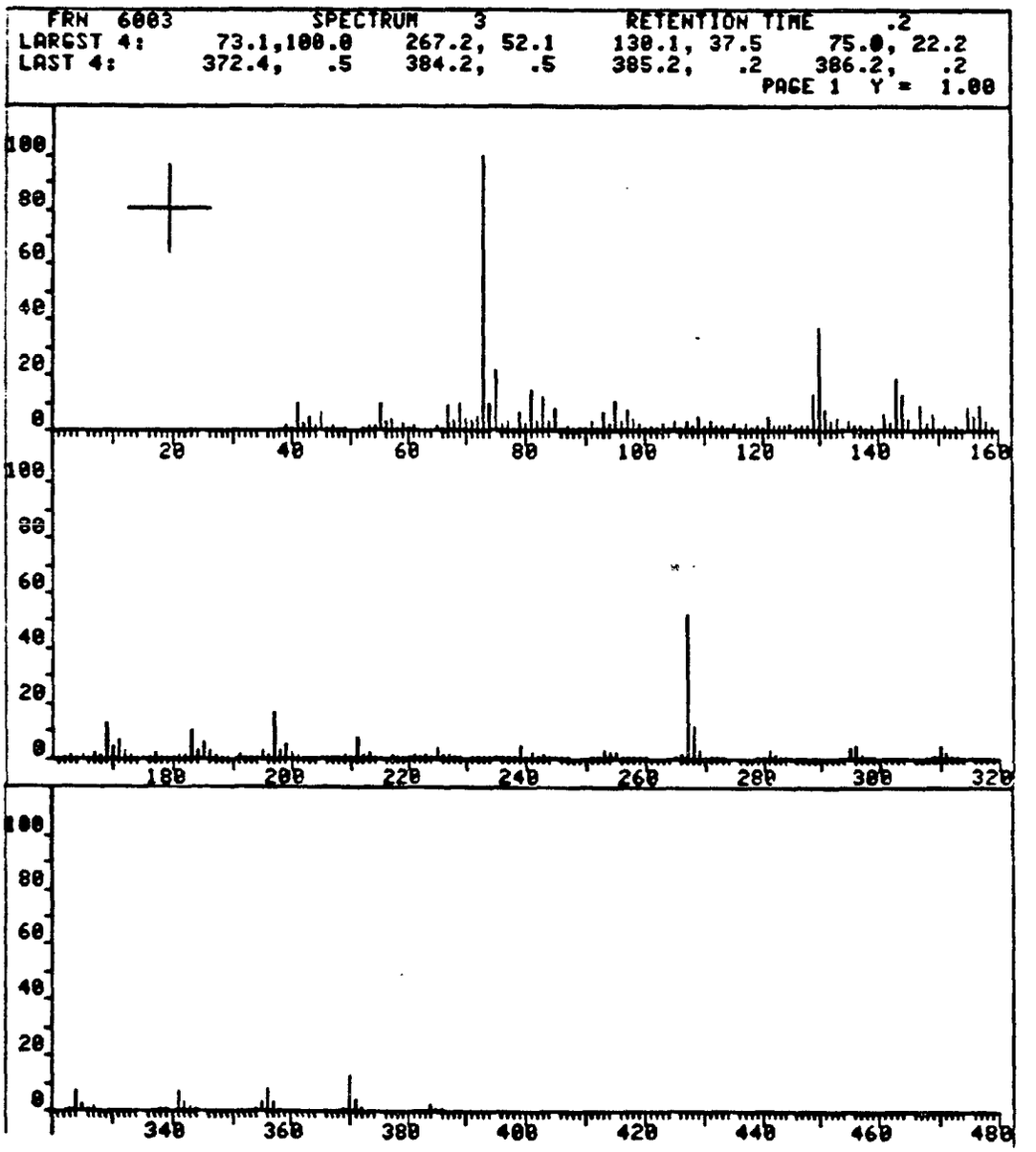
MASS	ABUND	MASS	ABUND	MASS	ABUND
244	.6	279	.6	356	.7
245	.6	281	3.3		
246	.4	282	3.4	399	.4
247	.6	283	1.7	>PAUSE	
248	.4	284	.5		
249	.8	285	.4		
250	.7				
251	.7	295	1.3		
252	.6	296	2.6		
253	3.5	297	.6		
254	.8	299	.4		
255	.6				
257	.9	313	.8		
258	.6	314	.5		
259	.4	325	1.3		
260	.5	327	2.4		
261	.4				
263	.4	328	1.6		
264	.6	329	.7		
265	.6	341	2.5		
267	4.3				
268	3.0	342	3.2		
269	.9	343	1.3		
271	.6	344	.6		
		354	1.2		
277	.4	355	1.7		

Mass Spectra No. 7

1,12-Bis(trimethylsilyoxy)bicyclo[10.1.0]tridecane



M.W.= 356



FRN 6003 SPECTRUM 3 RET. TIME = .2
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
39	1.6	69	10.1	94	2.1	119	2.0
40	.9	70	4.2	95	10.3	120	1.0
41	9.5	71	3.3	96	3.8	121	4.9
42	2.5	72	4.7	97	7.1	122	1.7
43	5.1	73	100.0	98	4.5	123	1.7
44	1.4	74	9.6	99	2.3	124	1.4
45	6.8	75	22.2	100	.8	125	2.5
46	.5			101	2.0	126	.7
47	1.4	76	2.4	102	.3	127	1.8
		77	3.8	103	2.2	128	2.0
48	.6	78	.8			129	12.6
49	.3	79	6.4	104	.7	130	37.5
52	.2	80	2.2	105	3.6	131	7.4
53	1.8	81	14.4	106	.6		
54	1.3	82	3.3	107	3.3	132	2.8
55	9.8	83	11.8	108	1.7	133	4.2
56	3.5	84	3.8	109	5.1	134	1.2
57	4.1	85	8.3	110	1.9	135	3.4
58	1.1	86	.9	111	3.0	136	1.9
59	2.1	87	1.6	112	2.0	137	1.4
60	.5	88	.4	113	2.0	138	1.0
61	1.3	89	.7	114	.7	139	1.6
				115	2.4	140	.9
65	1.8	90	.2	116	1.0	141	5.7
66	.8	91	3.6	117	2.5	142	2.2
67	8.9	92	1.2			143	18.6
68	2.9	93	6.2	118	.8	144	13.2
						<CONT>	

FRN 6003 SPECTRUM 3 RET. TIME = .2
>PAUSE

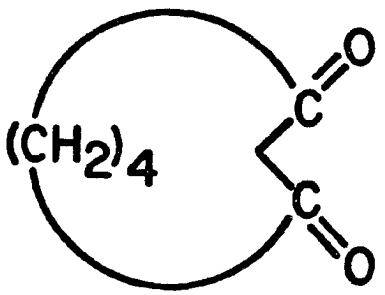
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
145	4.1	170	4.9	196	1.4	222	.4
		171	6.6	197	16.7	223	1.1
146	1.0	172	3.5	198	3.4	224	.5
147	9.3	173	1.2	199	5.4	225	4.0
148	2.7			200	2.0	226	1.0
149	5.7	174	.3	201	1.0	227	1.2
150	1.0	175	.6			228	.3
151	1.3	176	.5	202	.2	229	.3
152	.8	177	1.9	203	.4		
153	1.7	178	.4	204	.4	231	.4
154	.9	179	.6	205	.8	232	.2
155	8.2	180	.3	206	.2	233	.3
156	5.2	181	1.4	207	.9	234	.2
157	9.3	182	1.2	208	.3	235	.2
158	3.7	183	10.2	209	1.2	236	.2
159	1.3	184	2.9	210	.7	237	.8
		185	6.2	211	7.7	238	.5
160	.5	186	3.3	212	1.4	239	4.4
161	.7	187	1.1	213	2.0	240	.9
162	.3			214	.6	241	1.8
163	1.2	188	.2	215	.6	242	.4
164	.9	189	.4			243	1.3
165	1.0	191	1.1	217	1.4		
166	.5	192	.3	218	.8	244	.3
167	2.3	193	.7	219	.7	245	.7
168	1.0	194	.4	220	.5	246	.2
169	12.3	195	2.5	221	1.0	247	.3
						<CONT>	

FRM 6003 SPECTRUM 3 RET. TIME = .2

MASS	ABUND	MASS	ABUND	MASS	ABUND
251	.6	285	.2	354	.2
252	.8			355	.7
253	2.4	295	3.9		
254	1.9	296	4.6	356	2.1
255	1.8	297	1.1	357	.7
256	.4	298	.3	358	.2
257	.7	299	.2	369	.2
258	.3	309	.9	370	3.3
259	.4	310	4.3	371	1.0
260	.2	311	1.8	372	.5
265	.5	312	.6		
266	1.2	313	.2	384	.5
267	52.1			385	.2
268	11.8	323	.2	386	.2
269	3.2	324	1.7	>PAUSE	
270	.5	325	.5		
271	.8	326	.2		
		327	.3		
272	.2				
273	.2	338	.2		
279	.3	339	.2		
280	.3	341	1.8		
281	3.0				
282	.9	342	.9		
283	.6	343	.5		
284	.2	344	.2		

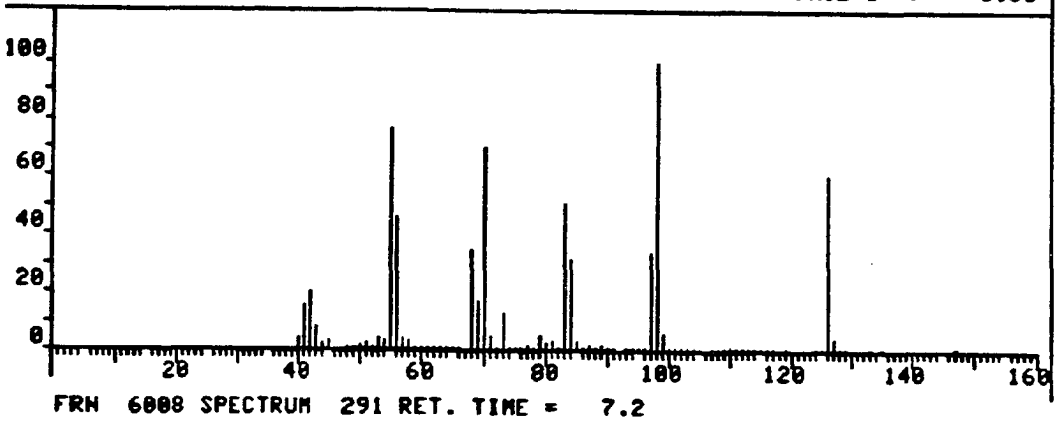
Mass Spectra No. 8

Cycloheptane-1,3-dione



M.W.=126

FRN 6008 SPECTRUM 291 RETENTION TIME 7.2
LARGST 4: 98.2,100.0 55.2, 76.3 70.1, 69.9 126.1, 60.8
LAST 4: 129.0, .2 132.9, .3 135.1, .2 147.1, .2
PAGE 1 Y = 1.00

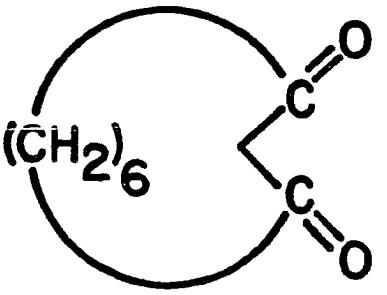


FRN 6008 SPECTRUM 291 RET. TIME = 7.2

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
40	4.6	66	1.1	93	.2	124	.2
		68	35.0	94	.2	125	.4
41	15.3	69	16.7	95	.4	126	60.8
42	19.9	70	69.9	96	.6	127	4.2
43	7.8	71	5.0	97	34.2	128	.7
44	2.7	72	1.1	98	100.0	129	.2
45	3.4	73	13.3	99	6.1		
		74	.9	100	.8	133	.3
48	.2	75	1.0	101	.5	135	.2
49	.4			102	.4		
50	1.6	76	.3	103	.8	147	.2
51	2.2	77	1.8			>PAUSE	
52	1.1	78	.3	104	.2		
53	4.1	79	5.3	105	.2		
54	3.0	80	2.5	107	.2		
55	76.3	81	3.7	108	.3		
56	45.8	82	1.1	109	.2		
57	4.6	83	50.5	110	.2		
58	3.8	84	31.4	111	.4		
59	1.2	85	2.9	112	.3		
60	.8	86	.7	113	.2		
61	.4	87	1.5	114	.4		
		88	.8	115	.2		
62	.4	89	1.8	116	.2		
63	.3			117	.2		
64	.2	90	.2				
65	1.0	91	.2	119	.2		

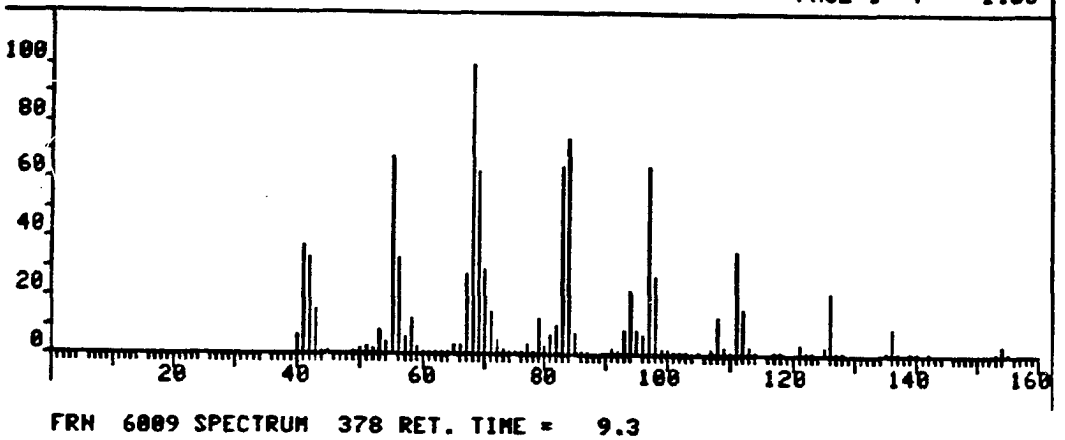
Mass Spectra No. 9

Cyclononane-1,3-dione



M.W.=154

FRN 6009 SPECTRUM 378 RETENTION TIME 9.3
LARGST 4: 68.0,100.0 84.1, 73.8 55.2, 67.7 97.1, 64.8
LAST 4: 142.1, .2 153.1, .2 154.1, 3.1 155.2, .3
PAGE 1 Y = 1.00

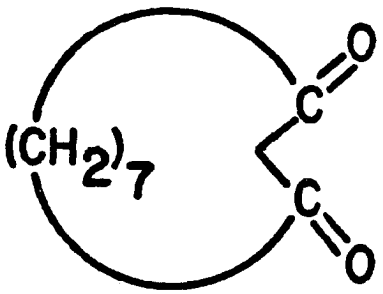


FRN 6009 SPECTRUM 378 RET. TIME = 9.3

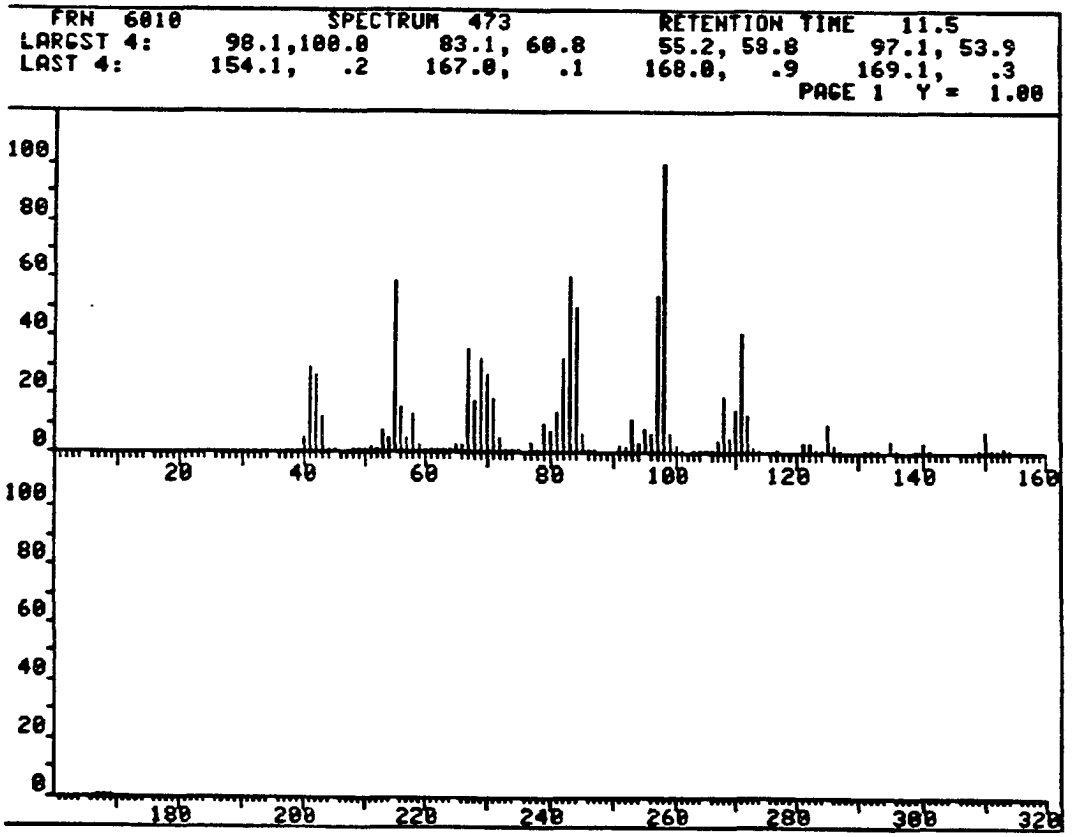
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
40	6.4	68	100.0	96	6.8	128	.2
41	36.9	69	62.8	97	64.8		
42	33.1	70	29.1	98	26.4	135	.8
43	15.5	71	14.4	99	1.7	136	9.1
44	.9	72	4.7	100	1.4	137	1.0
45	.7	73	1.3	101	.2	139	1.2
		74	.3	102	.1	140	.2
49	.1	75	.1	103	.1	142	.2
50	1.6						
51	2.2	76	.1	105	.1	153	.2
52	1.5	77	3.3	107	1.3	154	3.1
53	8.6	78	1.2	108	13.3	155	.3
54	4.4	79	11.8	109	2.6	>PAUSE	
55	67.7	80	2.6	110	1.0		
56	33.1	81	6.7	111	35.4		
57	5.9	82	10.1	112	15.0		
58	12.4	83	64.1	113	2.7		
59	2.2	84	73.8	114	.2		
60	.1	85	7.1	117	.1		
61	.2	86	.8				
		87	.2	118	.2		
62	.3			121	3.2		
63	.5	91	2.0	122	.3		
64	.2	92	1.1	123	.1		
65	2.8	93	8.2	125	2.4		
66	3.3	94	22.2	126	20.6		
67	27.6	95	8.6	127	1.2		

Mass Spectra No. 10

Cyclodecane-1,3-dione



M.W.=168

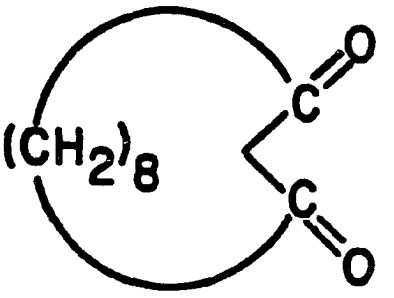


FRN 6010 SPECTRUM 473 RET. TIME = 11.5

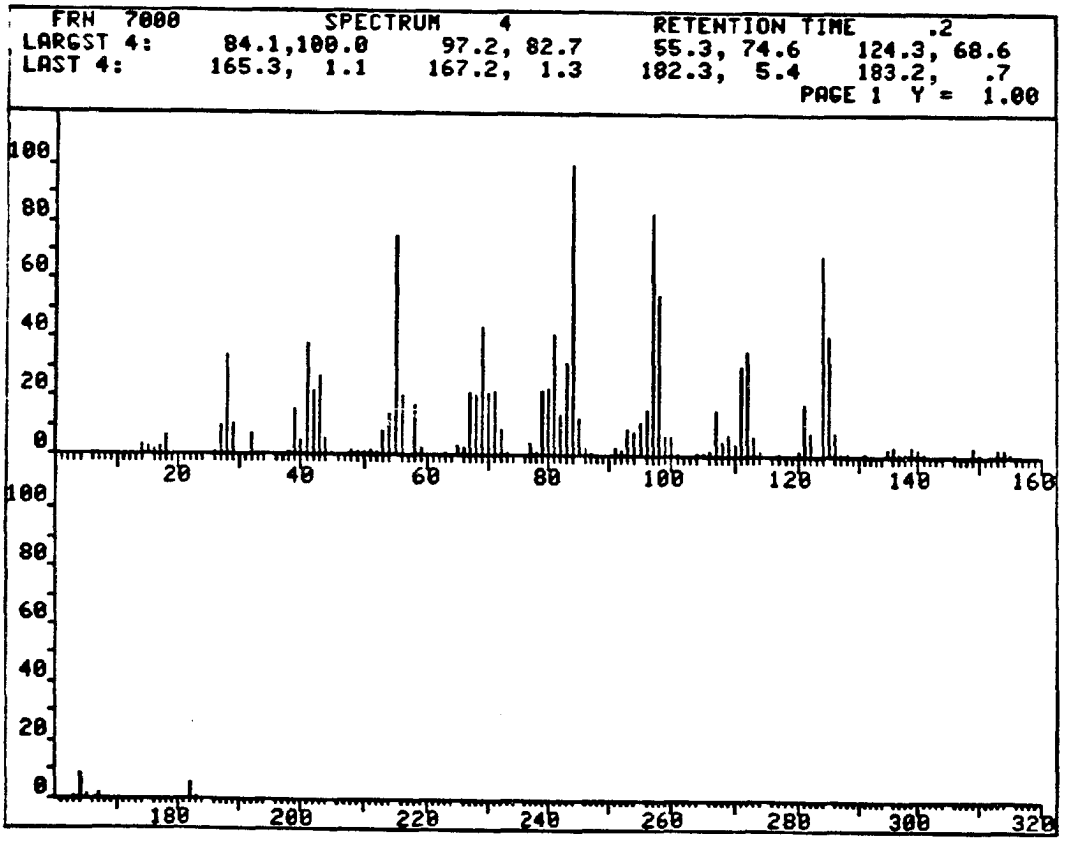
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
40	5.0	67	35.7	96	6.2	127	.3
41	28.8	68	17.7	97	53.9	131	.1
42	26.4	69	32.1	98	100.0		
43	12.4	70	27.0	99	6.7	132	.6
44	.7	71	18.7	100	2.1	133	.2
45	.5	72	5.4	101	.3	135	3.9
		73	1.0	103	.1	136	.5
48	.4	74	.2			139	.9
49	.1	75	.1	104	.2	140	2.9
50	.7			105	.3	141	.2
51	1.7	77	3.4	106	.7		
52	1.1	78	1.0	107	4.1	149	.7
53	7.6	79	9.6	108	19.3	150	7.0
54	5.4	80	7.2	109	5.0	151	.7
55	58.8	81	14.1	110	14.5	152	.1
56	15.4	82	32.1	111	41.6	153	1.6
57	5.2	83	60.8	112	13.5	154	.2
58	12.5	84	50.0	113	1.4		
59	2.2	85	6.5	114	.3	167	.1
60	.2	86	.8	117	.3	168	.9
61	.1	87	.2			169	.3
				121	2.9	>PAUSE	
62	.2	91	2.2	122	3.2		
63	.4	92	1.4	123	.4		
64	.2	93	11.0	124	.4		
65	2.4	94	3.2	125	9.5		
66	2.5	95	7.8	126	2.5		

Mass Spectra No. 11

Cycloundecane-1,3-dione



M.W.=182



FRN 7000 SPECTRUM 4 RET. TIME = .2
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
14	3.1	54	13.7	87	.6	120	1.8
15	2.3	55	74.6			121	17.7
16	2.0	56	19.8	91	2.1	122	7.8
17	2.7	58	17.3	92	1.5	124	68.6
18	6.5	59	2.6	93	9.1	125	40.6
				94	8.4	126	8.4
26	.8	63	.5	95	11.1	127	.7
27	9.8	65	3.1	96	15.4	128	.8
28	33.7	66	2.5	97	82.7	131	.5
29	10.8	67	21.2	98	54.6		
32	7.1	68	20.4	99	6.2	135	2.4
		69	43.7	100	6.4	136	3.0
38	.8	70	20.7	101	.8	137	.5
39	15.2	71	22.1			138	.7
40	5.1	72	9.1	104	.7	139	3.8
41	37.6	73	1.0	105	1.0	140	2.7
42	22.4			106	1.6	141	.7
43	26.9	77	4.0	107	15.4		
44	5.9	78	1.3	108	5.1	146	.9
45	1.0	79	22.0	109	7.3	149	3.3
		80	23.1	110	4.4	150	.6
48	1.6	81	40.7	111	30.7	153	2.2
49	.8	82	13.8	112	35.1	154	2.1
50	.4	83	31.7	113	6.4	155	.4
51	1.6	84	100.0	114	1.3		
52	1.2	85	13.0	117	.4	163	.4
53	8.0	86	2.1			164	8.7
						<CONT>	

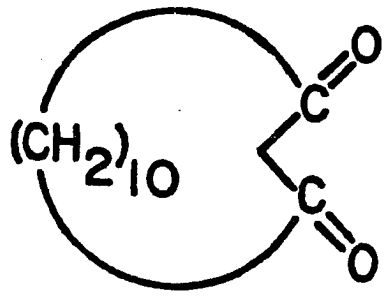
FRN 7000 SPECTRUM 4 RET. TIME = .2

MASS	ABUND
165	1.1
167	1.3
182	5.4
183	.7

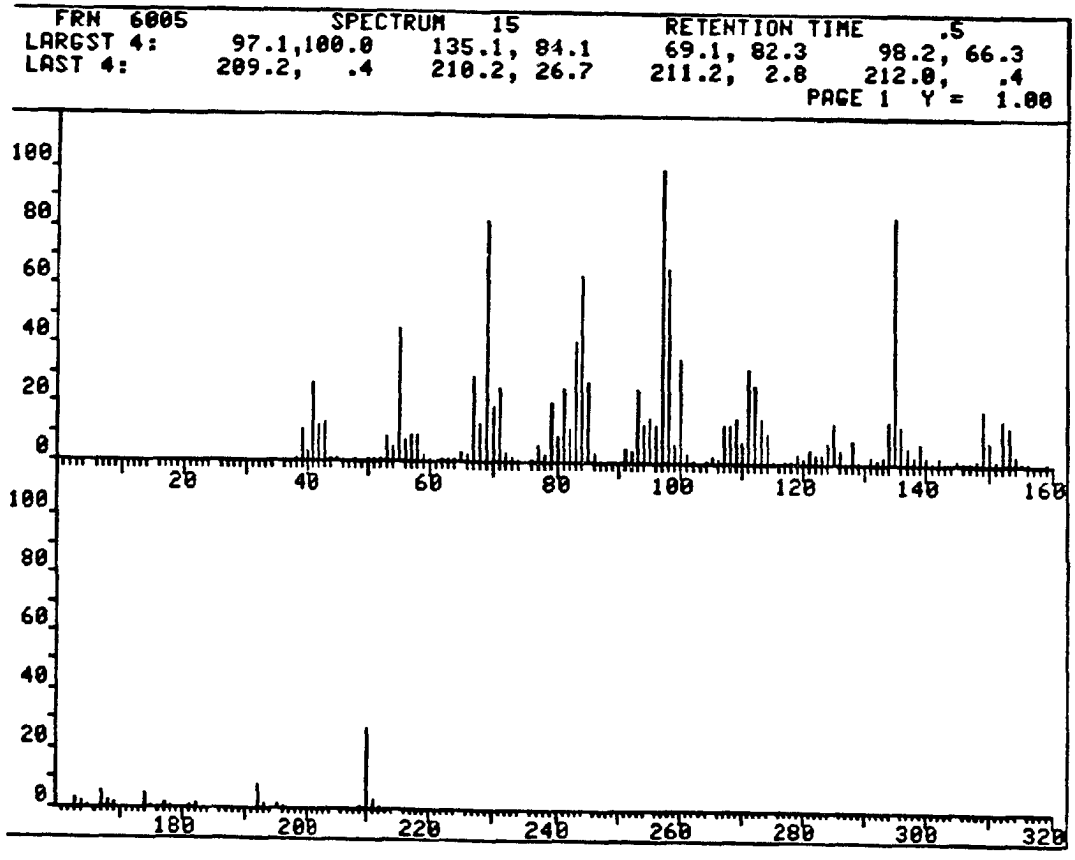
>PAUSE

Mass Spectra No. 12

Cyclotridecane-1,3-dione



M.W.=210



FKN 6005 SPECTRUM 15 KEV. TIME = .5
>PAUSE

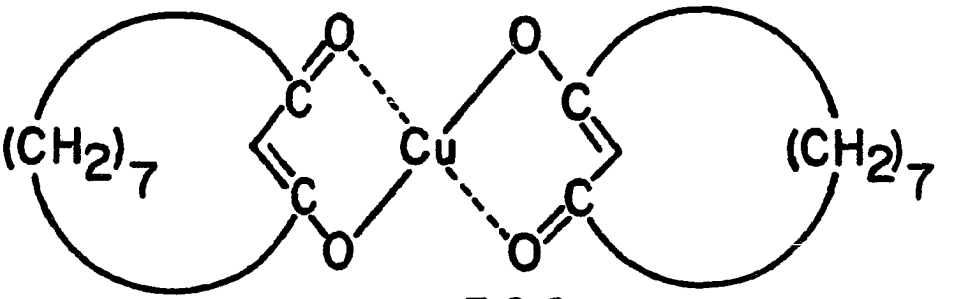
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
38	.5	67	29.1	96	13.3	123	3.5
39	10.7	68	12.9	97	100.0	124	7.3
40	3.9	69	82.3	98	66.3	125	13.9
41	26.4	70	19.1	99	6.2	126	5.0
42	11.7	71	25.0	100	35.7	128	8.5
43	12.5	72	3.9	101	3.3	129	.8
44	.7	73	1.4	102	.4	131	2.7
45	.8	74	.2				
				104	.6	132	1.8
48	.3	76	.3	105	2.5	133	2.3
50	.4	77	5.6	106	2.0	134	14.4
51	1.2	78	2.3	107	12.6	135	84.1
52	1.2	79	19.9	108	13.5	136	12.8
53	8.5	80	9.1	109	15.5	137	6.0
54	5.0	81	24.7	110	7.5	138	2.5
55	44.9	82	11.2	111	32.1	139	7.6
56	7.6	83	41.6	112	27.0	140	2.1
57	9.3	84	63.5	113	15.2	141	1.1
58	9.3	85	27.5	114	10.6	142	2.7
59	2.2	86	3.4	115	.9	143	.3
60	.2	87	.8	117	.7	145	1.7
62	.2	91	4.8	118	.4	146	.8
63	.3	92	4.0	119	2.8	147	.4
64	.3	93	25.3	120	1.8	148	1.4
65	3.7	94	12.5	121	5.2	149	18.9
66	2.8	95	15.2	122	3.2	150	7.8
						<CONT>	

FKN 6005 SPECTRUM 15 KEV. TIME = .5

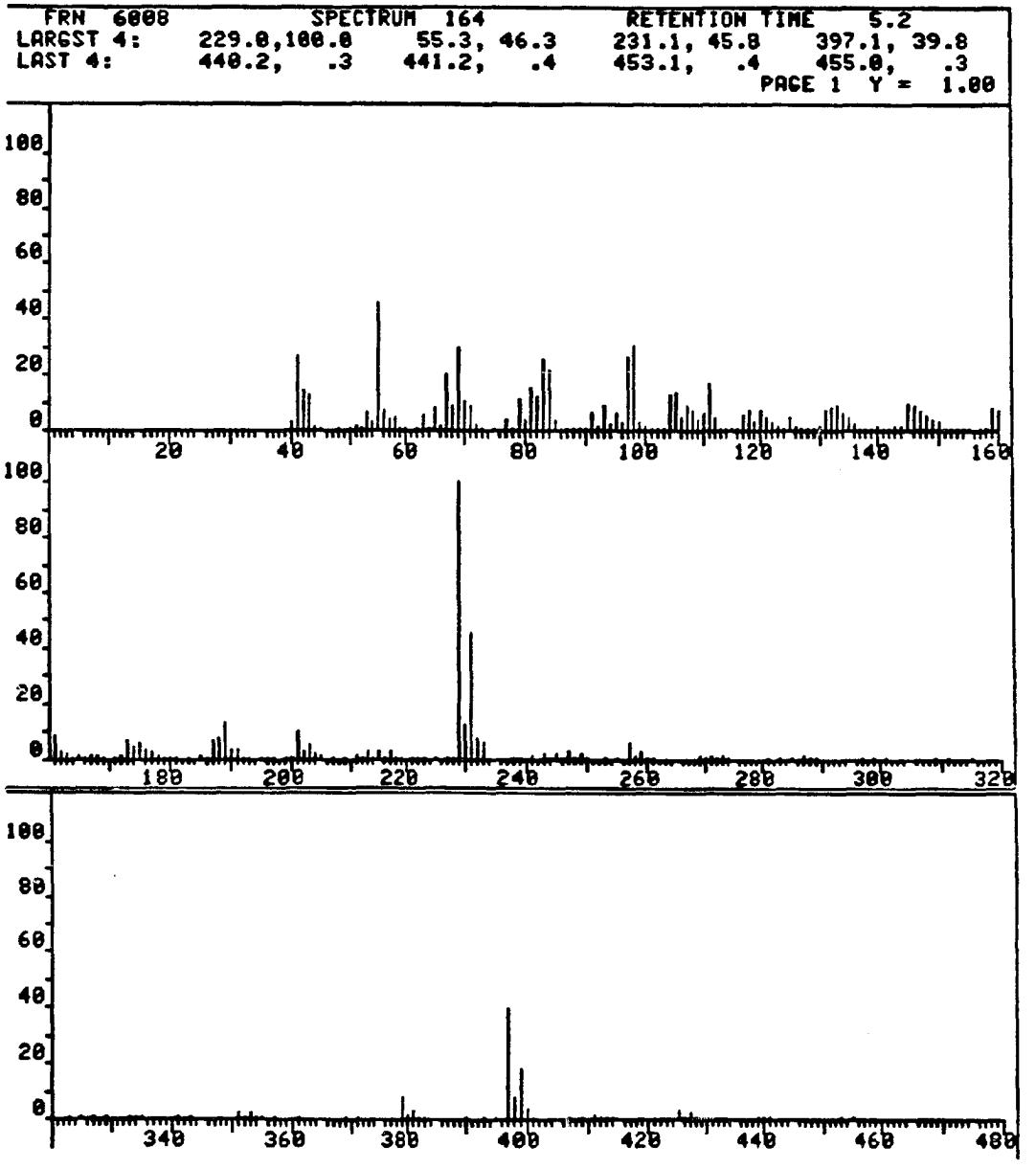
MASS	ABUND	MASS	ABUND
151	1.8	209	.4
152	15.3	210	26.7
153	12.8	211	2.8
154	2.9	212	.4
155	.7	>PAUSE	
156	.2		
159	.7		
163	3.5		
164	1.8		
165	.4		
167	5.0		
168	1.8		
169	1.1		
174	4.9		
175	.6		
177	1.6		
178	.2		
181	.8		
182	1.2		
192	8.0		
193	1.3		
195	1.4		
196	.3		

Mass Spectra No. 13

Bis(cyclodecane-1,3-dionato)copper(II)



M.W.=398



FRN 6008 SPECTRUM 164 RET. TIME = 5.2
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
40	3.8	69	30.1	96	3.3	121	5.1
41	26.7	70	10.5	97	26.4	122	2.8
42	14.9	71	9.1	98	30.7	123	2.0
43	13.2	72	2.1	99	2.9	124	1.0
44	1.9	73	.9	100	1.4	125	5.3
45	.7	75	.2	101	.4	126	1.4
				102	.3	127	.5
48	.2	77	4.4	103	1.1	128	.5
50	.6	78	1.1			129	1.2
51	1.4	79	11.1	104	13.2	130	1.4
52	.9	80	4.3	105	13.9	131	7.5
53	6.7	81	15.0	106	5.3		
54	3.1	82	11.8	107	8.8	132	7.7
55	46.3	83	26.1	108	7.5	133	9.3
56	7.6	84	21.7	109	3.9	134	6.7
57	4.3	85	4.0	110	6.2	135	5.1
58	5.1	86	.5	111	16.9	136	2.5
59	1.0	87	.3	112	5.3	137	1.2
60	.3	88	.2	113	1.0	138	.7
		89	.9	114	.3	139	1.0
62	.3			115	.4	140	1.4
63	5.8	90	.9	116	.6	141	1.0
64	.4	91	6.8	117	5.8	142	.3
65	7.7	92	1.8			143	1.5
66	2.0	93	9.2	118	7.1	144	1.4
67	20.5	94	2.3	119	3.8	145	10.2
68	8.7	95	6.7	120	7.2		
						<CONT>	

FRN 6008 SPECTRUM 164 RET. TIME = 5.2
>PAUSE

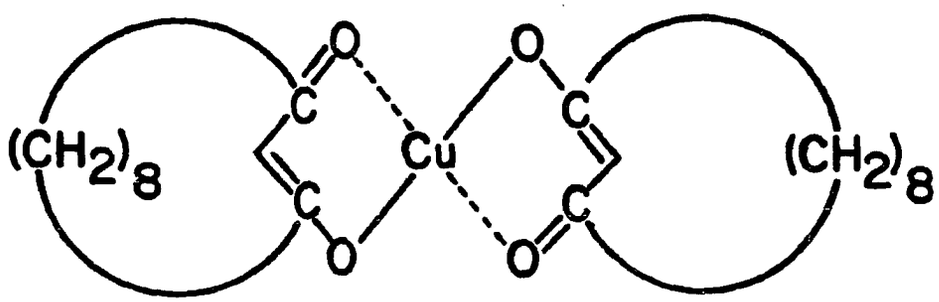
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
146	9.2	174	4.8	203	5.1	234	.6
147	7.2	175	6.4	204	1.8	238	.2
148	5.6	176	3.9	205	1.1	239	.4
149	4.3	177	3.0	207	.4	241	1.1
150	3.7	178	1.0	209	.5	243	2.3
151	.8	179	.3	211	1.2		
152	.4	180	.4	212	.3	244	.6
153	1.1	181	.5	213	2.6	245	2.3
154	.4	183	.6	214	.4	246	.4
155	.6	185	1.0	215	3.4	247	3.0
157	.9	186	.3			248	.7
158	.6	187	7.2	216	.9	249	1.7
159	8.6			217	2.6	250	.3
		188	8.2	218	.4	253	.4
160	7.2	189	13.5	219	.8	255	.3
161	8.5	190	3.6	221	.5	257	6.3
162	3.1	191	4.1	222	.3		
163	1.9	192	.8	223	.4	258	1.0
164	.7	193	.4	225	.4	259	3.3
165	.9	195	.3	227	.9	260	.6
166	.6	196	.4	228	.4	261	.9
167	1.1	197	.5	229	100.0	269	1.4
168	1.4	199	.8			270	.3
169	.7	200	.5	230	12.6	271	1.6
171	.7	201	9.8	231	45.8		
172	1.4			232	7.8	272	.5
173	7.2	202	3.1	233	6.1	273	1.2
						<CONT>	

FRH 6008 SPECTRUM 164 RET. TIME = 5.2

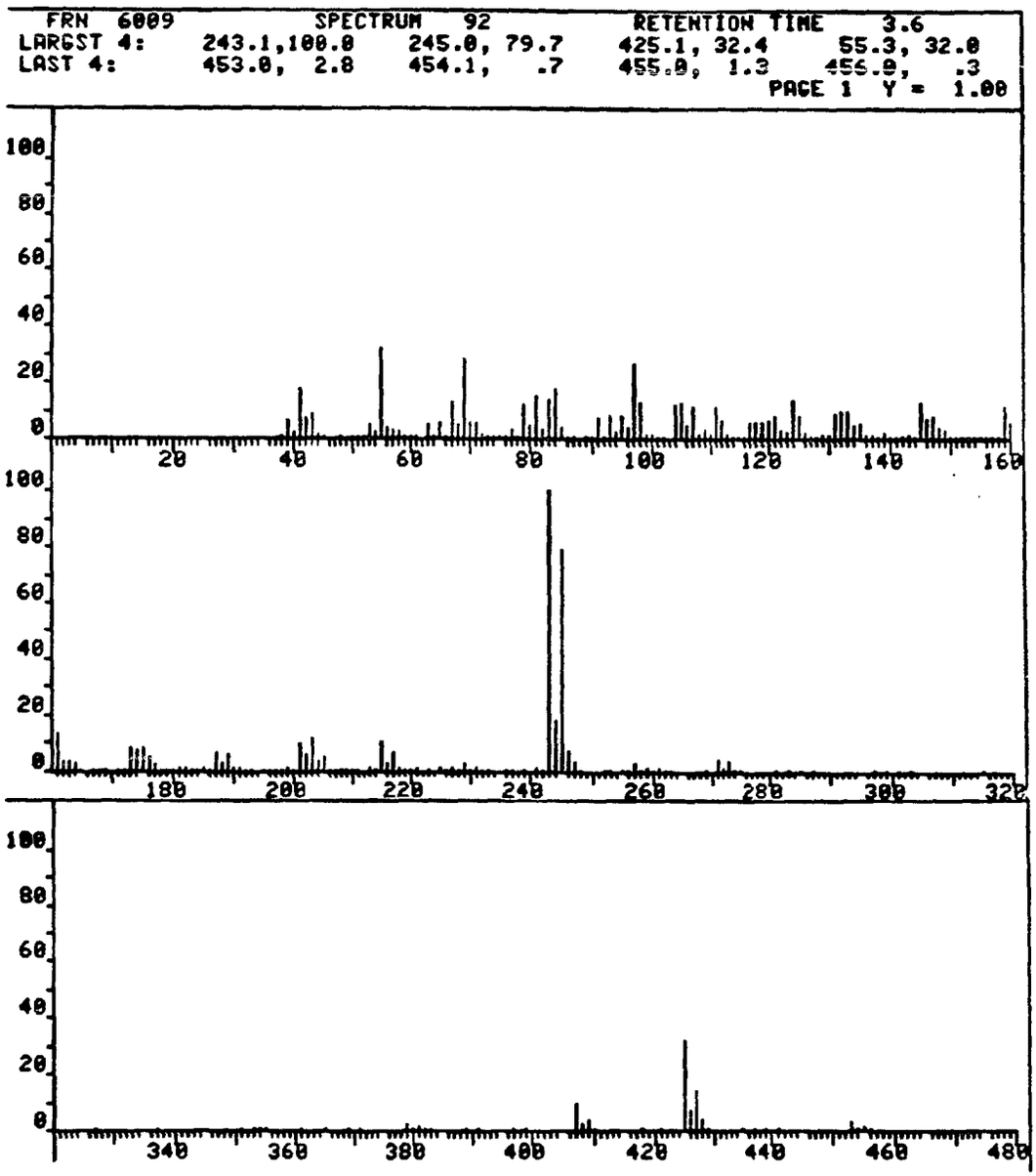
MASS	ABUND	MASS	ABUND	MASS	ABUND
274	.2	351	2.8	409	.6
281	.6	352	.6	411	1.6
283	.4	353	2.1		
285	.6	354	.5	412	.4
		355	.4	413	.8
287	1.3			414	.2
288	.3	357	.3	425	3.9
289	.7	361	.5		
297	.4	369	.9	426	.9
299	.4			427	2.2
		371	.6	428	.5
301	.5	379	8.5	439	1.0
309	.3	380	1.5		
311	.2	381	3.6	440	.3
		382	.6	441	.4
315	.6	383	.3	453	.4
323	.4				
325	.6	390	.4	455	.3
327	.4	393	.5	>PAUSE	
		395	.4		
329	.3	397	39.8		
333	1.0				
334	.2	398	8.0		
335	.2	399	18.8		
341	.3	400	4.0		
		401	.7		
343	.2	407	1.0		

Mass Spectra No. 14

Bis(cycloundecane-1,3-dionato)copper(II)



M.W.= 426



FRN 6009 SPECTRUM 92 RET. TIME = 3.6
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
38	.4	67	12.9	93	7.8	119	5.6
39	6.4	68	4.7	94	2.8	120	6.8
40	2.1	69	28.5	95	8.0	121	8.0
41	17.8	70	5.5	96	4.3	122	3.5
42	7.0	71	6.0	97	26.4	123	2.2
43	9.3	72	1.3	98	12.9	124	14.2
44	1.5	73	.7	99	1.6	125	8.4
45	.5	74	.3	100	1.9	126	2.1
		75	.2	101	.4	127	.4
48	.2			102	.5	128	.7
50	.5	76	.6			129	1.4
51	1.0	77	3.7	104	12.2	130	1.7
52	.6	78	.9	105	13.2	131	8.9
53	4.9	79	11.9	106	5.1		
54	2.5	80	5.0	107	11.3	132	9.5
55	32.0	81	15.5	108	2.0	133	9.9
56	4.5	82	3.2	109	3.6	134	5.0
57	3.7	83	14.2	110	1.5	135	5.6
58	2.4	84	17.7	111	11.4	136	2.0
59	.7	85	4.1	112	6.5	137	1.3
60	.2	86	.6	113	1.6	138	.3
61	.2	87	.3	114	.5	139	2.4
		89	1.0	115	.6	140	.9
63	5.0			116	.5	141	1.0
64	.3	90	.7	117	6.1	142	.4
65	5.7	91	7.4			143	1.6
66	1.2	92	1.2	118	5.9	144	1.2
						<CONT>	

FRN 6009 SPECTRUM 92 RET. TIME = 3.6
>PAUSE

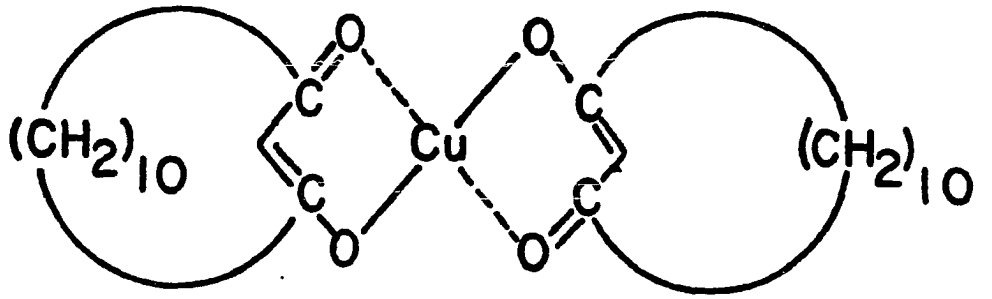
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
145	13.1	172	.6	198	.3	226	.3
		173	8.9	199	1.3	227	1.6
146	7.1			200	.5	228	.3
147	7.7	174	8.3	201	10.5	229	3.3
148	4.6	175	8.5				
149	3.7	176	5.1	202	5.9	230	.6
150	1.0	177	3.4	203	11.7	231	1.2
151	.5	178	.6	204	4.3	232	.3
152	.4	179	.3	205	5.1	233	.4
153	1.1	180	.3	206	.7	236	.2
154	.8	181	1.5	207	.4	237	.3
155	.7	182	1.3	208	.2	239	.3
156	.3	183	.4	209	.3	241	1.2
157	1.2	184	.2	210	.5	242	.5
158	1.0	185	1.0	211	.3	243	100.0
159	11.2	186	.4	213	1.1		
		187	7.0	214	.3	244	18.5
160	5.8			215	10.6	245	79.7
161	13.3	188	2.8			246	8.2
162	3.9	189	5.8	216	3.3	247	4.1
163	4.0	190	1.2	217	6.9	248	.8
164	2.9	191	1.0	218	1.4	252	.2
165	.7	192	.5	219	.6	253	.2
167	.7	193	.3	220	.2	255	.6
168	.4	195	.5	221	1.0	256	.3
169	.4	196	.2	223	.4	257	2.9
171	.8	197	.8	225	1.3		
						<CONT>	

FRN 6009 SPECTRUM 92 RET. TIME = 3.6

MASS	ABUND	MASS	ABUND	MASS	ABUND
258	.4	337	.2	418	.2
259	1.8			421	.2
260	.4	351	.2	425	32.4
261	1.6	353	.3		
262	.3	354	.3	426	7.1
263	.5	355	.4	427	14.5
269	.4			428	3.9
271	4.9	361	.2	429	.5
		365	.2	435	.5
272	1.8	369	.2	437	.3
273	4.8			439	.9
274	.5	371	.2		
275	.3	379	2.7	441	.4
281	.2	380	.6	453	2.8
283	.5	381	1.5		
285	.7	382	.2	454	.7
		383	.3	455	1.3
287	.2			456	.3
297	.3	389	.5	>PAUSE	
299	.3	391	.2		
		397	.7		
301	.9				
303	.3	399	.3		
		407	9.7		
315	.2	408	2.4		
327	.2	409	4.2		
		410	.9		

Mass Spectra No. 15

Bis(cyclotridecane-1,3-dionato)copper(II)



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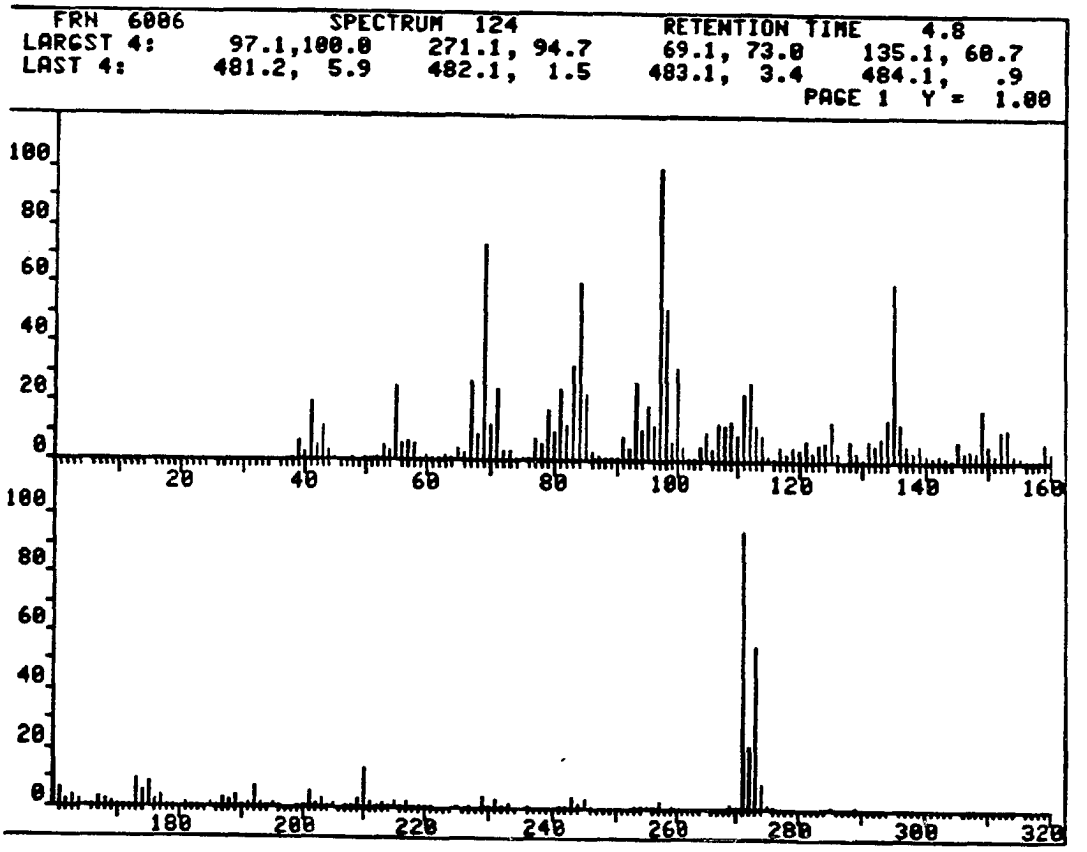
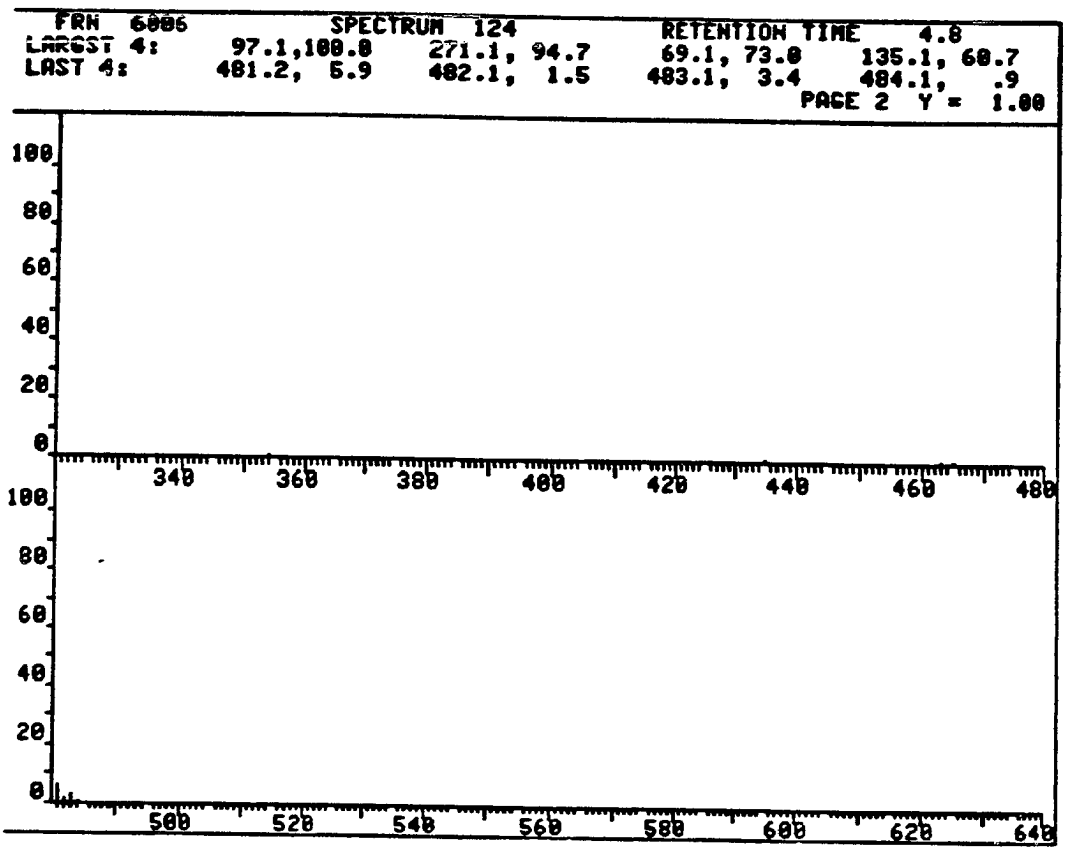




FRN 6006 SPECTRUM 124 RET. TIME = 4.8
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
38	.4	66	2.2	91	8.0	117	4.7
39	6.4	67	26.7	92	4.1		
40	2.5	68	9.4	93	26.7	118	2.6
41	19.3	69	73.0	94	10.6	119	5.2
42	5.2	70	11.9	95	19.1	120	4.0
43	11.3	71	23.9	96	12.2	121	6.9
44	3.0	72	3.6	97	100.0	122	3.2
45	.9	73	3.7	98	51.7	123	5.9
		74	.6	99	6.7	124	6.3
48	.3	75	.4	100	31.0	125	14.1
50	.5			101	4.6	126	3.2
51	1.2	76	1.0	102	.8	128	6.9
52	1.1	77	7.0	103	1.1	129	3.2
53	4.9	78	5.9			130	1.0
54	2.9	79	17.5	104	5.3	131	7.1
55	25.0	80	9.8	105	9.9		
56	5.6	81	23.9	106	4.5	132	5.9
57	6.6	82	12.2	107	12.9	133	8.0
58	5.7	83	32.8	108	12.4	134	14.5
59	1.2	84	60.1	109	13.9	135	60.7
60	1.3	85	22.9	110	8.8	136	12.9
61	.4	86	3.8	111	22.7	137	5.9
		87	1.8	112	26.7	138	2.9
62	.3	88	.5	113	12.4	139	5.5
63	1.8	89	.9	114	9.4	140	2.3
64	.8			115	1.8	141	1.8
65	4.3	90	.4	116	.7	142	2.4

<CONT>

FRN 6006 SPECTRUM 124 RET. TIME = 4.8
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
143	1.4	168	1.8	195	.9	227	.4
144	.7	169	1.2	196	.4	229	3.6
145	7.4	170	.3	199	.8		
		171	.6	200	.3	230	.5
146	3.2	172	.6	201	5.6	231	2.4
147	4.5	173	9.7			232	.8
148	2.9			202	1.0	233	1.1
149	18.3	174	5.6	203	3.5	236	.3
150	6.0	175	8.4	204	.6	241	.5
151	2.5	176	1.8	205	1.1	242	.3
152	10.4	177	3.7	207	.7	243	4.0
153	11.3	178	.5	208	.5		
154	2.1	179	.4	209	2.4	244	1.0
155	1.3	181	1.2	210	13.8	245	2.7
156	.5	182	.8	211	1.8	246	.4
157	1.3	183	.5	212	.3	253	.8
158	.5	185	1.1	213	1.1	254	.3
159	6.4	186	.3	214	.3	255	.6
		187	3.1	215	2.1	256	.6
160	3.1					257	1.9
161	5.9	188	1.7	216	.9		
162	2.0	189	4.0	217	1.7	259	.7
163	3.8	190	.8	218	.4	269	1.0
164	2.1	191	1.1	219	.4	270	.6
165	.7	192	6.9	220	.3	271	94.7
166	.4	193	1.2	221	.3		
167	3.2	194	.4	225	.4	272	21.2
						<CONT>	

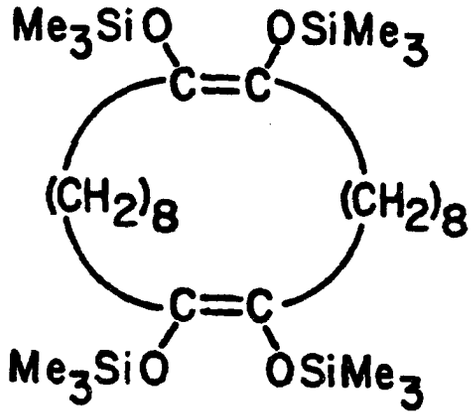
FRN 6006 SPECTRUM 124 RET. TIME = 4.8

MASS	ABUND
273	55.1
274	8.9
275	1.4
276	.4
285	.3
289	.3
354	.4
435	.3
463	.9
465	.3
481	5.9
482	1.5
483	3.4
484	.9

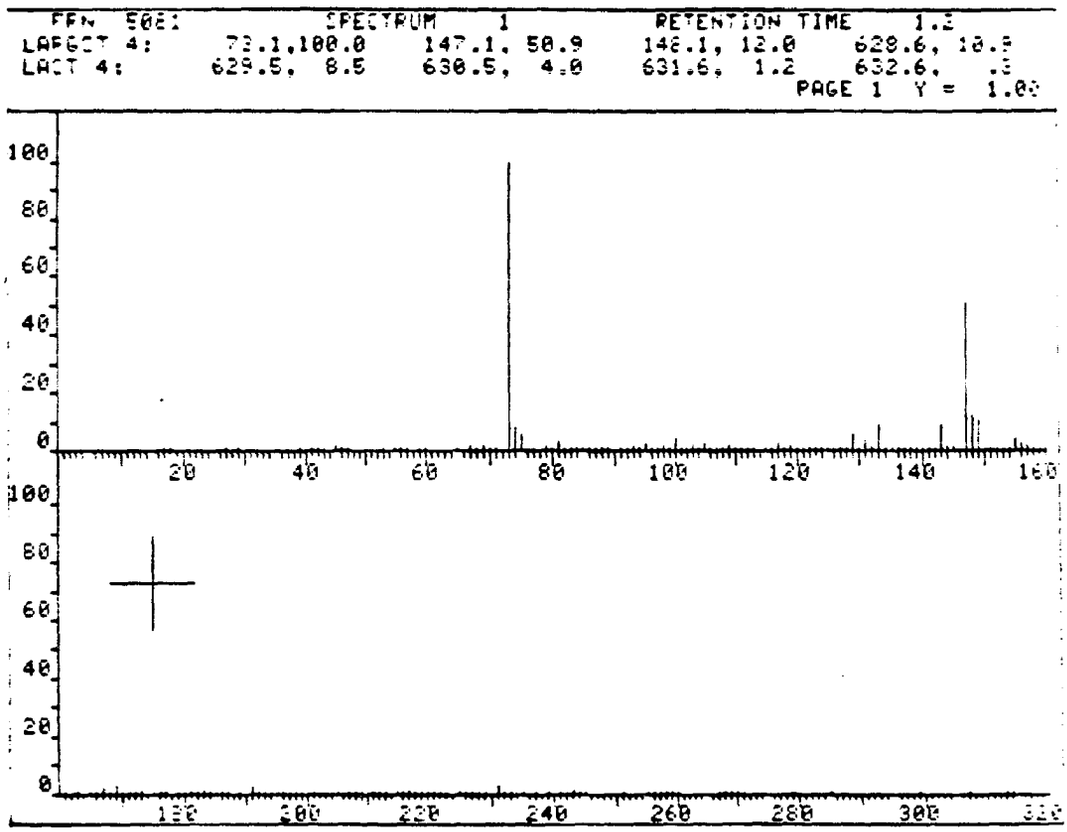
>PAUSE

Mass Spectra No. 16

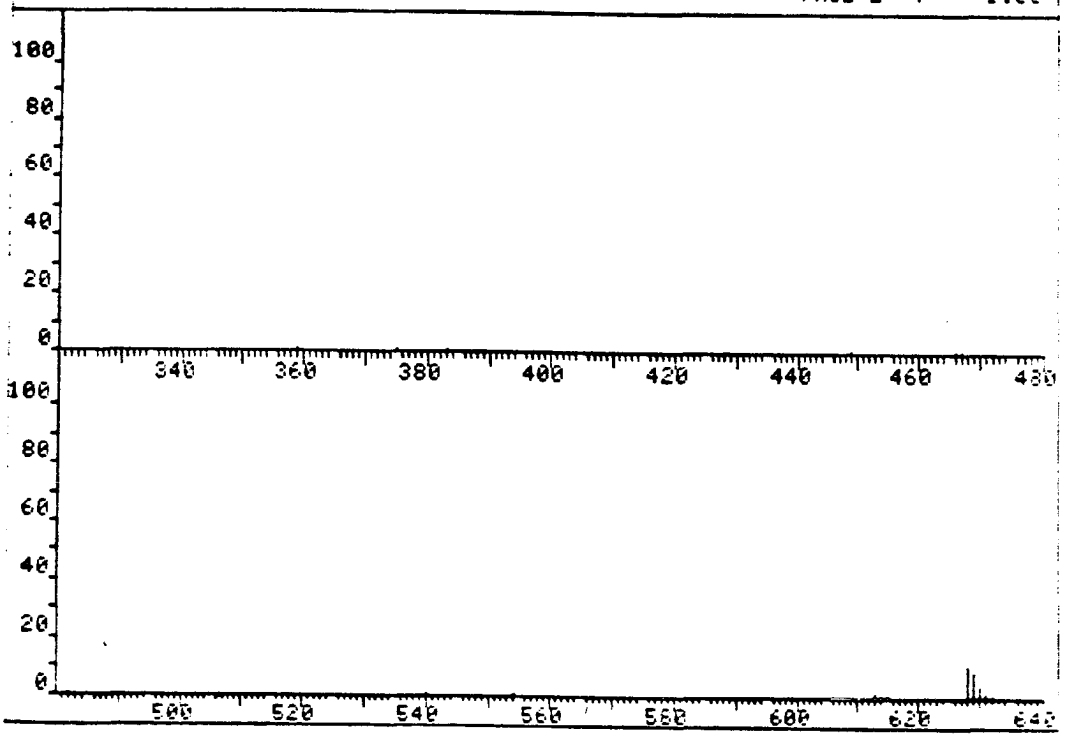
Tetrakis(trimethylsiyloxy)cycloeicosadiene



M.W.=628



```
  FPN  5081          SPECTRUM    1          RETENTION TIME    1.2
LARGST 4:     73.1,100.0    147.1, 50.9    148.1, 12.0    628.6, 10.9
LAST 4:      629.5,  8.5    630.5,  4.0    631.6,  1.2    632.6,   .3
                                                  PAGE 2  Y =  1.00
```



FPN 5081 SPECTRUM 1 RET. TIME = 1.2
PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
17	.1	73	100.0	100	4.1	126	.2
18	.4	74	7.9	101	1.0	127	.8
		75	5.7	102	.2	128	.6
27	.1			103	1.4	129	5.5
28	.0	76	.9			130	.9
		77	1.0	104	.4	131	4.0
39	.2	79	1.6	105	2.2		
41	.4	80	.5	106	.3	132	1.4
42	.2	81	3.9	107	1.1	133	9.4
43	1.0	82	.5	108	.5	134	1.3
45	1.8	83	1.1	109	1.3	135	1.0
46	.1	84	.9	110	.2	136	.7
47	.2	85	1.2	111	.9	137	.6
		86	.3	112	.5	138	1.3
53	.2	87	.3	113	.5	139	.9
55	1.1	88	.2	115	1.0	140	.3
56	.1	89	.1	116	.4	141	1.2
57	.9			117	2.1	142	.8
59	.4	91	.9			143	9.0
60	.4	92	.5	118	.4	144	1.4
		93	2.0	119	1.3	145	2.0
65	.0	94	.3	120	.5		
67	1.8	95	2.2	121	.9	147	50.9
68	.3	96	.5	122	.4	148	12.0
69	1.7	97	1.2	123	.2	149	10.3
70	.7	98	1.7	124	.3	150	1.0
71	.6	99	.7	125	1.2	151	1.0

(CONT)

FRN 5081 SPECTRUM 1 RET. TIME = 1.2
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
152	.2	181	1.1	211	.2	243	1.6
153	.8	182	.4	212	.1		
154	.5	183	1.3	213	.3	244	.5
155	4.6	184	.5	215	.9	245	.3
156	2.2	185	.8			251	.2
157	2.1	186	.1	216	.2	255	.9
158	.4	187	.3	217	1.2	256	.2
159	.5			218	.9	257	.8
		189	.3	219	.6		
160	.2	191	1.9	220	.2	258	.2
161	.4	192	.4	221	.9	259	.2
163	.3	193	.5	222	.2	260	.1
165	.8	194	.2	223	.7	267	.2
166	.6	195	.7	225	.4	268	.2
167	1.7	196	.3	226	.1	269	.3
168	.7	197	.8	227	.3	270	.2
169	3.5	198	.2	228	.1	271	.3
170	.8	199	.4	229	.4		
171	.8	201	.3			279	.3
172	.2			231	2.6	285	.3
173	1.1	202	.2	232	.4		
		203	.3	233	.3	299	.3
175	.2	204	.2	235	.2		
176	.2	205	.3	237	.2	307	.2
177	.6	207	.5	239	.2	313	.4
179	.3	208	.2	241	.2		
180	.4	209	.6	242	.6	314	3.5
						<CONT>	

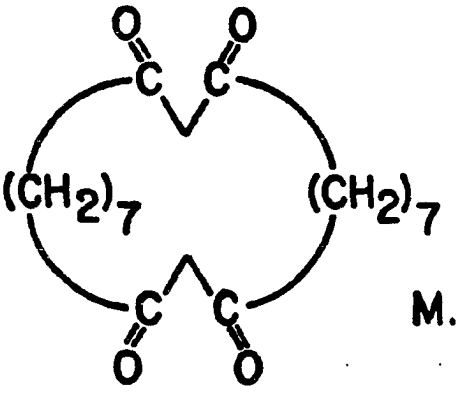
FRN 5081 SPECTRUM 1 RET. TIME = 1.2

MASS	ABUND
359	.2
375	.2
383	.1
449	.1
466	.7
467	.3
482	.2
540	.2
554	.2
613	1.1
614	.7
615	.3
628	10.9
629	8.5
630	4.0
631	1.2
632	.3

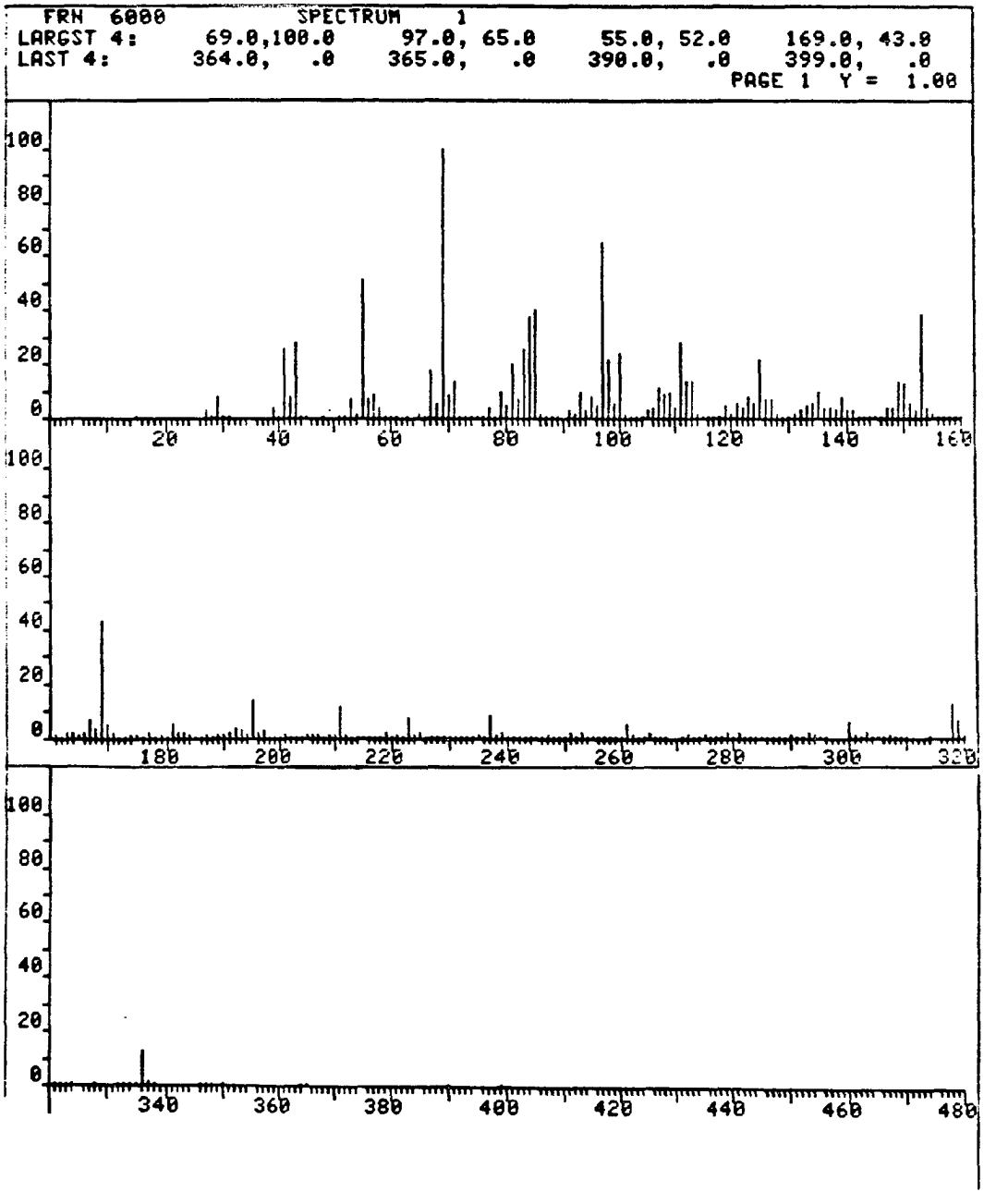
>PAUSE

Mass Spectra No. 17

Cycloeicosane-1,3,11,13-tetraone



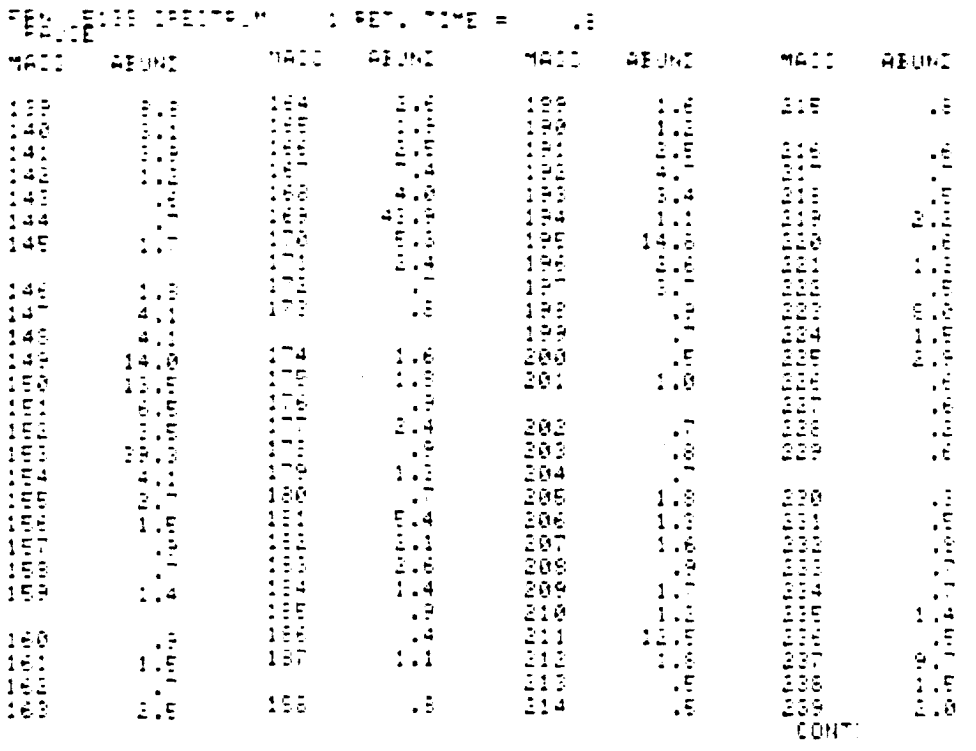
M.W.= 336



FRN E138 SPECTRUM 1 RET. TIME = .8
PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
15	.2	61	.5	88	.3	114	2.4
				89	.4	115	.3
27	3.2	63	.6			116	1.0
28	.7	65	2.7	91	3.2	117	1.9
29	8.5	66	1.7	92	2.5		
30	.3	67	18.0	93	10.1	118	.5
31	.9	68	6.9	94	3.9	119	5.5
		69	100.0	95	8.4	120	2.3
39	4.9	70	9.2	96	5.1	121	6.7
40	1.7	71	14.6	97	65.2	122	4.0
41	26.4	72	1.4	98	22.7	123	8.6
42	8.2	73	1.0	99	6.7	124	6.6
43	28.2	74	.4	100	24.1	125	22.6
44	.8	75	.1	101	2.3	126	7.2
45	.9			102	.2	127	7.3
		76	.3	103	.4	128	2.3
48	.4	77	4.3			129	.7
51	.3	78	.8	104	.9	130	1.3
52	.5	79	10.5	105	3.3	131	2.4
53	7.0	80	5.1	106	4.7		
54	2.6	81	20.2	107	11.5	132	3.9
55	52.3	82	7.2	108	9.3	133	5.7
56	7.5	83	26.9	109	10.6	134	6.0
57	9.9	84	38.6	110	4.9	135	10.6
58	4.8	85	40.1	111	28.7	136	4.6
59	1.5	86	2.2	112	14.6	137	4.1
60	.5	87	.7	113	14.1	138	3.6

<CONT>

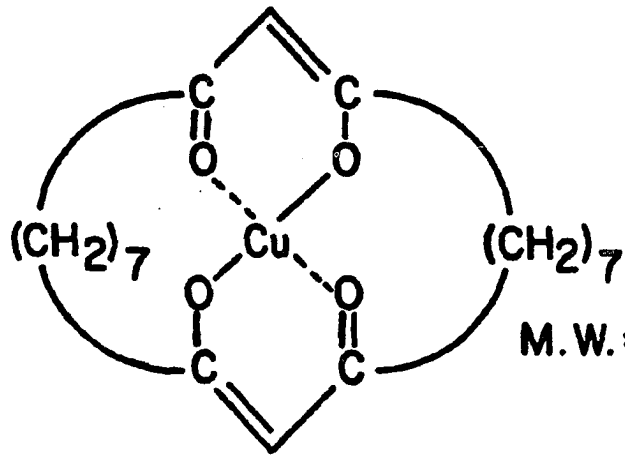


FRN 5138 SPECTRUM : RET. TIME = .8

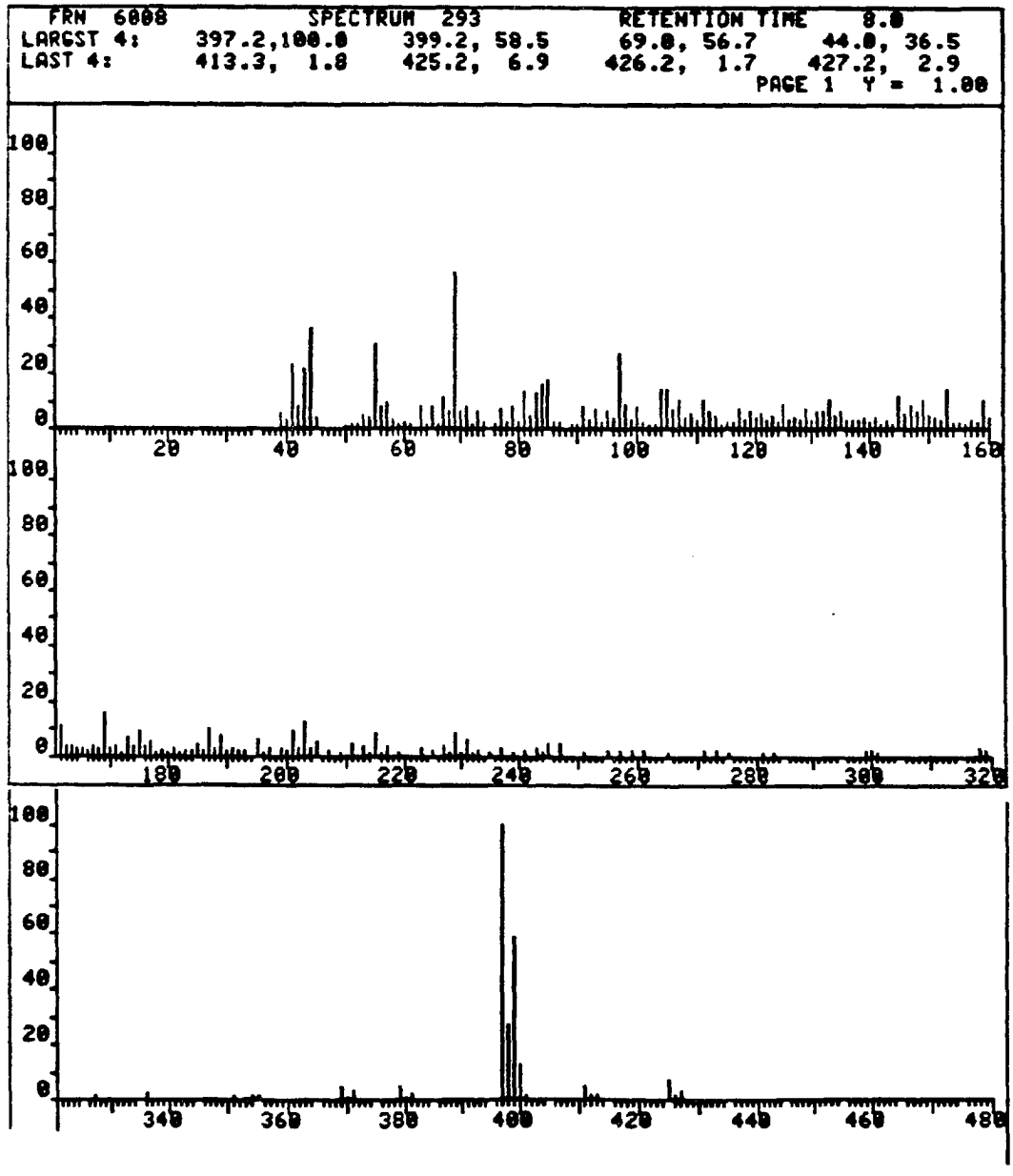
MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUNI
240	.6	265	2.0	292	.2	328	.4
241	.2	266	.4	293	2.9	332	.3
243	.2	267	.3	294	1.5	333	.3
242	.8	268	.4	295	.7	334	.3
		271	.4	296	.3	335	.3
244	.4					336	13.6
245	.5	272	1.3	300	6.7	337	2.6
246	.2	273	.4	301	1.9	339	.4
247	1.5	274	.2	302	.3		
248	.6	275	1.7	303	2.0	346	.5
249	.5	276	.8	304	.8	347	.3
250	.1	277	.4	305	.2	348	.2
251	.2	278	.3	306	.2	350	.3
252	.7	279	2.8	307	1.1		
253	.2	280	.8	308	.4	364	.3
254	.6	281	2.4	309	.2	365	.2
255	.3	282	.9	310	.2		
256	.3	283	.4			390	.3
257	.7	284	.2	314	.3		
		285	.4	318	13.8	399	.3
258	.4			319	7.7	*PAUSE	
259	.4	286	.3	320	1.2		
260	.3	287	.2	321	1.3		
261	.1	288	.2	322	.3		
262	.1	289	.8	323	.2		
263	.1	290	1.2	324	.2		
264	.4	291	.4				

Mass Spectra No. 18

(Cycloeicosane-1,3,11,13-tetraonato)copper(II)



M.W. = 398



FRM 6000 SPECTRUM 293 RET. TIME = 8.0
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
39	5.9	69	56.7	96	4.6	121	6.1
40	3.8	70	6.5	97	27.3	122	2.9
41	23.4	71	8.4	98	8.9	123	4.6
42	7.7	72	1.4	99	3.3	124	2.8
43	21.9	73	6.5	100	8.0	125	9.0
44	36.5	74	2.2	101	2.1	126	2.9
45	4.3			102	1.3	127	4.0
		76	1.7	103	1.6	128	3.5
50	1.2	77	6.9			129	7.2
51	1.6	78	2.4	104	14.8	130	3.1
52	1.8	79	8.5	105	14.7	131	6.7
53	4.8	80	2.5	106	7.2		
54	4.0	81	14.2	107	10.2	132	6.8
55	30.7	82	4.9	108	4.1	133	10.3
56	7.6	83	12.7	109	5.8	134	5.3
57	9.6	84	16.1	110	2.9	135	6.7
58	3.4	85	17.7	111	10.8	136	2.9
59	1.6	86	2.7	112	6.2	137	3.0
60	2.4	87	2.3	113	4.9	138	3.4
61	1.8	89	1.3	114	1.3	139	4.6
				115	2.7	140	2.1
63	8.3	90	1.5	116	2.1	141	4.3
64	1.4	91	8.7	117	7.5	142	1.7
65	8.7	92	3.1			143	3.5
66	1.6	93	7.1	118	3.0	144	1.9
67	11.6	94	2.4	119	6.7	145	11.7
68	6.3	95	6.6	120	4.2		

<CONT>

FRM 6000 SPECTRUM 293 RET. TIME = 8.0
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
146	6.1	172	1.6	199	3.4	233	1.8
147	9.2	173	7.1	200	1.8	235	1.2
148	6.5			201	9.5	237	3.2
149	10.6	174	4.0			239	1.6
150	5.2	175	9.2	202	2.8	241	2.0
151	4.3	176	3.6	203	12.1	243	2.9
152	3.0	177	5.2	204	2.7		
153	14.3	178	1.3	205	5.2	244	1.2
154	2.1	179	1.9	207	2.1	245	4.9
155	2.8	180	1.2	209	1.3	247	4.4
156	1.5	181	2.9	211	4.5	251	1.2
157	3.3	182	1.6	213	4.0	255	1.9
158	2.6	183	2.2	214	1.2	257	2.1
159	10.2	184	1.7	215	8.8		
		185	4.5			259	2.3
160	4.6	186	1.7	216	1.4	261	1.9
161	11.1	187	10.1	217	4.0	265	1.3
162	3.8			219	1.5	271	1.7
163	3.7	188	2.6	223	2.9		
164	2.8	189	8.3	225	2.0	273	2.3
165	3.1	190	2.1	227	4.1	275	1.5
166	2.1	191	3.4	228	1.2	281	1.3
167	3.9	192	2.2	229	9.0	283	1.3
168	2.6	193	2.1				
169	15.7	195	6.1	230	1.6	299	2.0
170	2.6	196	1.4	231	6.3		
171	3.8	197	2.8	232	1.5	300	1.9

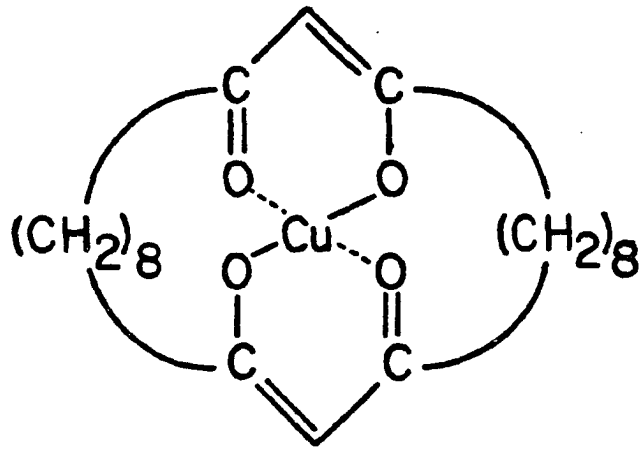
<CONT>

FRM 6008 SPECTRUM 293 RET. TIME = 8.0

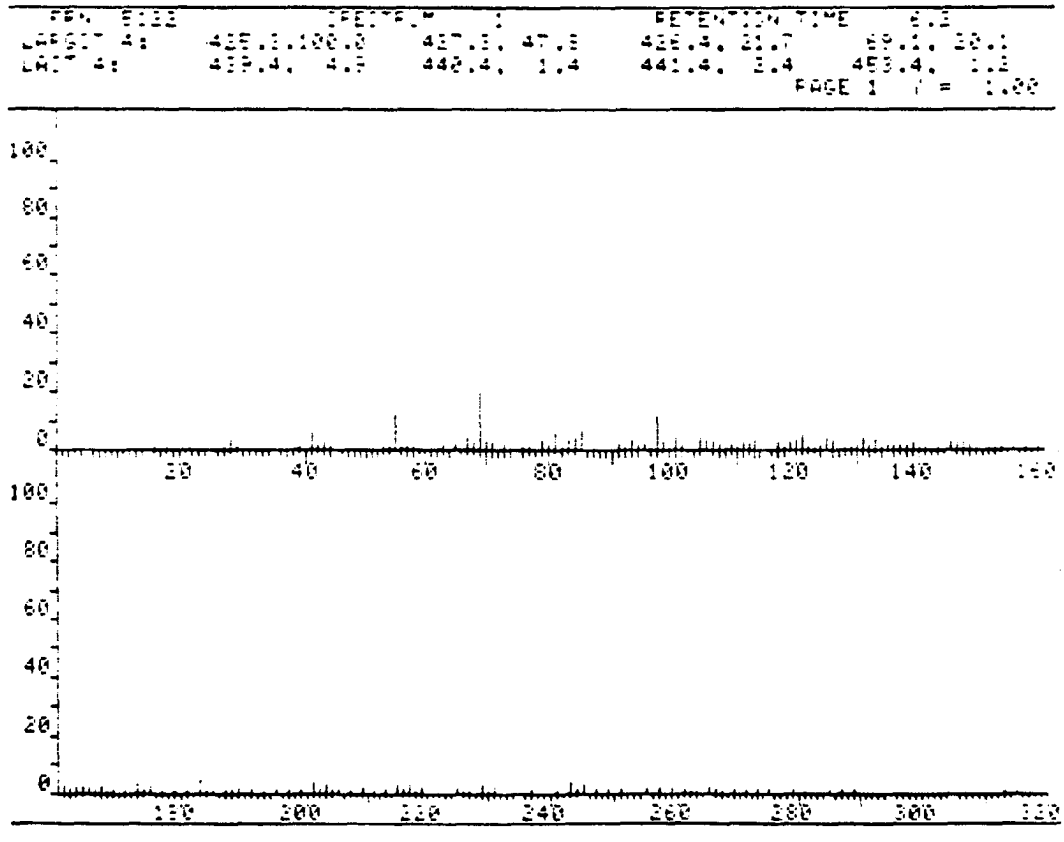
MASS	ABUND	MASS	ABUND
301	1.2	411	5.2
318	3.5	412	1.3
319	1.9	413	1.8
327	1.3	425	6.9
336	2.3	426	1.7
		427	2.9
351	2.8	>PAUSE	
353	1.2		
354	1.7		
355	1.7		
369	5.4		
370	1.3		
371	2.9		
379	4.6		
380	1.2		
381	2.5		
397	100.0		
398	27.3		
399	58.5		
400	12.8		
401	1.7		

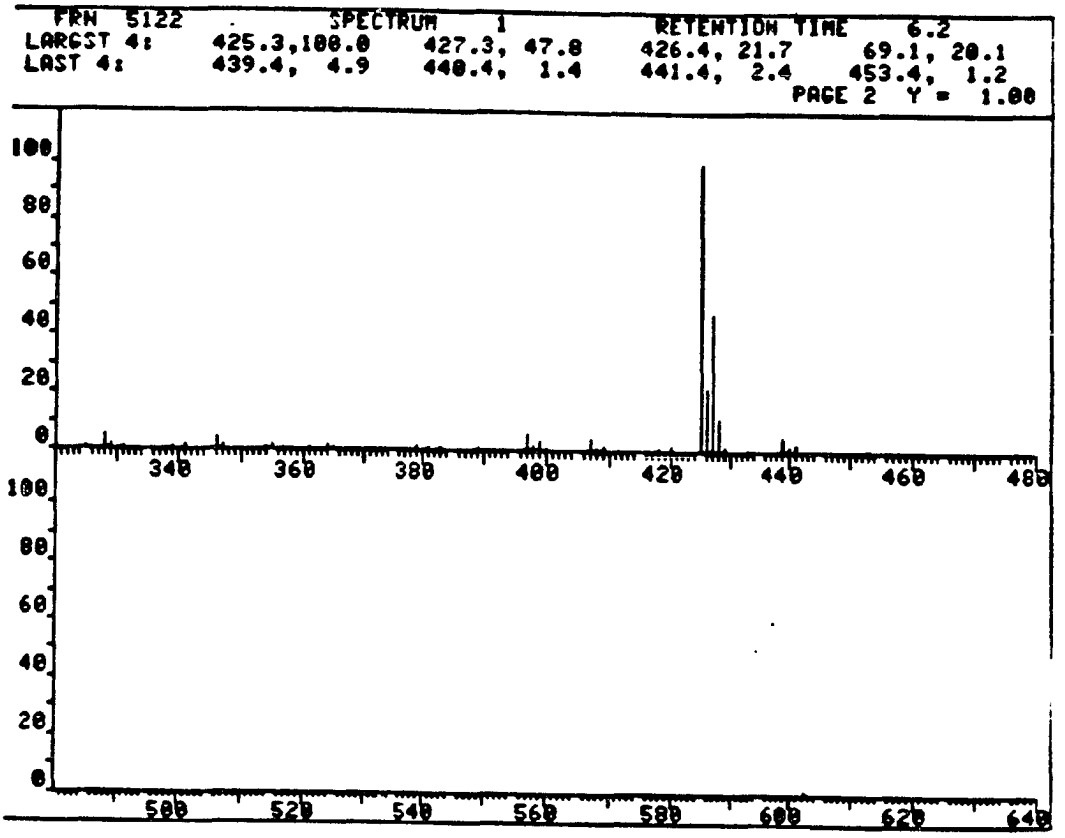
Mass Spectra No. 19

(Cyclodocosane-1,3,12,14-tetraonato)copper(II)



M.W. = 426





FRN 5122 SPECTRUM 1 RET. TIME = 6.2
PAGE 2

MASS	REL INT	MASS	REL INT	MASS	REL INT	MASS	REL INT
73	1.9	107	2.6	136	1.5		
		108	1.0	137	1.1		
		109	1.9	138	1.6		
		110	.4	139	.5		
		111	.5	140	.3		
		112	2.0	141	2.0		
		113	2.1	143	1.6		
		117	2.4	145	3.3		
		118	1.0	146	2.4		
		119	2.2	147	.3		
		120	2.9	148	2.3		
		121	4.0	151	1.6		
		122	1.6	152	1.2		
		123	.8	153	1.4		
		124	1.7	155	1.1		
		125	2.1	157	1.7		
		126	2.1	159	2.6		
		128	1.9				
		129	1.8	160	2.2		
		130	1.4	161	3.2		
100	4.7	131	4.4	162	2.0		
101	1.3			163	1.9		
		132	1.4	164	1.7		
104	4.0	133	3.0	165	1.9		
105	3.3	134	1.6	166	1.1		
106	3.1	135	2.4	167	3.1		

CONT

FRN 5122 SPECTRUM 1 RET. TIME = 6.2
>PAUSE

MASS	ABUND	MASS	ABUND	MASS	ABUND	MASS	ABUND
168	1.3	205	1.4	255	1.2	328	4.7
169	1.4	207	1.0	257	1.7	329	1.7
171	1.2	209	2.3			331	.9
173	3.9	211	1.0	259	2.0	339	1.1
		213	1.1	261	1.7	341	1.3
174	1.5	215	2.4	262	.9		
175	2.5			263	.9	346	4.5
177	.3	216	1.0	265	2.1	347	1.9
179	1.1	217	3.8	266	1.0	354	.1
181	1.9	218	.9	267	1.2	355	1.4
183	6.8	219	2.0	269	1.3		
184	1.6	225	2.0	271	1.4	361	.9
185	1.4	226	.9			364	1.6
187	1.2	227	.9	273	1.0	365	.9
		229	3.3	275	1.0		
188	1.3			279	1.2	379	1.3
189	2.1	230	.9	281	.9	381	1.0
191	1.0	231	2.1	285	1.2	383	1.1
193	.9	237	1.3				
195	1.4	241	1.2	287	1.4	389	.9
197	1.4	243	3.6	289	1.3	397	5.7
199	1.3						
201	4.0	244	1.0	313	1.4	398	1.6
		245	2.4			399	3.2
202	1.2	247	1.2	315	1.0	400	.9
203	2.7	249	1.0	325	1.2	407	4.0
204	1.1	251	1.4			408	.9

>CONT

FRN 5122 SPECTRUM 1 RET. TIME = 6.2

MASS	ABUND
409	1.8
418	.9
420	1.4
425	100.0
426	21.7
427	47.8
428	11.1
429	1.7
439	4.9
440	1.4
441	2.4
453	1.2

>PAUSE

VITA

Thomas Charles Taylor was conceived, born, and raised in Muleshoe on the high plains of Texas. The date of his birth was March 1, 1953. He attended elementary and high school in Muleshoe and then attended McMurry College in Abilene, Texas. He received a Bachelor of Arts degree from McMurry in May, 1975.

He married the former Cathy Lynn Mardis in August of 1972. They have a son, Nicholas Charles, who was born October 21, 1978. His wife is also from Muleshoe, Texas and a graduate of McMurry College.

He entered graduate school at Louisiana State University in August of 1975 and is presently a candidate for the degree of Doctor of Philosophy. He is a member of the American Chemical Society, Gamma Sigma Epsilon and Phi Lambda Upsilon.

EXAMINATION AND THESIS REPORT

Candidate: Thomas Charles Taylor

Major Field: Analytical Chemistry

Title of Thesis: SYNTHESIS AND CHARACTERIZATION OF MACROCYCLIC-1,3-DIKETONES AND THEIR METAL CHELATES

Approved:

Eugene W. Berg
Major Professor and Chairman

James D. Ingraham
Dean of the Graduate School

EXAMINING COMMITTEE:

Edward McLaughlin

Frank C. Couttenye

H.N. Rabinowitz

D.K. Carpenter

Date of Examination:

June 10, 1981